

THIS REPORT HAS BEEN DELIMITED  
AND CLEARED FOR PUBLIC RELEASE  
UNDER DOD DIRECTIVE 5200.20 AND  
NO RESTRICTIONS ARE IMPOSED UPON  
ITS USE AND DISCLOSURE.

DISTRIBUTION STATEMENT A

APPROVED FOR PUBLIC RELEASE;  
DISTRIBUTION UNLIMITED.

AD918253

**HIGH STRENGTH, THERMALLY STABLE  
POLYMERIC FIBERS**

Chadwick B. Delano  
R. Randolph Doyle  
Robert J. Milligan  
WHITTAKER CORPORATION

TECHNICAL REPORT AFML-TR-74-22  
February 1974



Distribution limited to U.S. Government agencies only; test and evaluation; August 1973. Other requests for this document must be referred to the Air Force Materials Laboratory, Nonmetallic Materials Division, Composite and Fibrous Materials Branch, AFML/MBC, Wright-Patterson Air Force Base, Ohio 45433.

Air Force Materials Laboratory  
Air Force Systems Command  
Wright-Patterson Air Force Base, Ohio

## NOTICE

When Government drawings, specifications, or other data are used for any purpose other than in connection with a definitely related Government procurement operation, the United States Government thereby incurs no responsibility nor any obligation whatsoever; and the fact that the government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data, is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use, or sell any patented invention that may in any way be related thereto.

Copies of this report should not be returned unless return is required by security considerations, contractual obligations, or notice on a specific document.

**HIGH STRENGTH, THERMALLY STABLE  
POLYMERIC FIBERS**

Chadwick B. Delano  
R. Randolph Doyle  
Robert J. Milligan

Distribution limited to U.S. Government agencies only; test and evaluation; August 1973. Other requests for this document must be referred to the Air Force Materials Laboratory, Nonmetallic Materials Division, Composite and Fibrous Materials Branch, AFML/MBC, Wright-Patterson Air Force Base, Ohio 45433.

## FOREWORD

This technical report was prepared by Whittaker Corporation, Research and Development Division, under US Air Force Contract No. F33615-72-C-1458. The work was administered under the direction of the Nonmetallic Materials Division, Air Force Materials Laboratory, with Mr. W. H. Gloor (AFML/MBC) as the Project Engineer.

This report covers the work conducted from 1 July 1972 to 1 September 1973. It is submitted in partial fulfillment of the contract and is catalogued by Research and Development Division as Report No. MJO 3039.

This program was performed in the Polymer Research Department, under the direction of Chadwick B. Delano, Principal Investigator. Those assisting were Robert J. Milligan and R. Randolph Doyle, Research Chemists, Technician support was provided by James B. Bott and William A. Tappen, Research Technicians.

This report was submitted by the author in January 1974.

This technical report has been reviewed and is approved for publication.



THEODORE G. REINHART, JR., Chief  
Composite and Fibrous Materials Branch  
Nonmetallic Materials Division  
Air Force Materials Laboratory

## ABSTRACT

The subject program has been concerned with the synthesis of specifically ordered heterocyclic polymer systems for evaluation as high tenacity fiber candidates. Specifically sought in the performance spectrum of successful fibers was a high level of mechanical properties, high energy absorption (work-to-break) and high temperature performance. The primary structural criteria for polymer order were: chain growth which describes a straight line; the absence of bulky pendant groups; capability for approaching a planar structure and interchain bonding. These structural features, which are primarily responsible for providing enhanced thermal and mechanical capability relative to non-oriented counterparts, at the same time render the polymer system highly intractable. The exception to these criteria appears to be the formation of the sought rod geometry through appropriate solvation of macromolecules containing flexible links to obtain for instance a helix.

Efforts with the poly-2,5(6)benzimidazole (AF-R-56) did not produce a yarn whose properties exceeded the previous contract yarn strengths of: as spun T/E/Mi = 7.4 gpd/30%/97 gpd; drawn T/E/Mi = 13.2/2.2/501. It is thought that low solids content dopes used in yarn formation present peculiar difficulty in the attainment of a higher strength yarn. Achievement of higher solids concentration in the dopes for yarn formation should provide enhanced yarn properties from the AF-R-56.

This solids "barrier" problem is solved when liquid crystalline behavior can be achieved with the macromolecules since the viscosity of solution reduces with increasing solids concentration in the anisotropic state. Efforts to induce the AF-R-56 into liquid crystalline behavior showed only slight promise.

## TABLE OF CONTENTS

<u>Section</u>		<u>Page</u>
I	OBJECTIVES AND SUMMARY OF RESULTS . . . . .	1
	Program Objectives . . . . .	1
	Summary of Results . . . . .	1
II	TECHNICAL DISCUSSION . . . . .	3
	The AF-Y-56 System . . . . .	3
	A. Spinning Solution Studies . . . . .	3
	B. SDO Wet Spinning Studies on Optimization of Fiber Properties . . . . .	9
	C. Heat Stretching and Fiber Studies . . . . .	14
	Modifications of the AF-R-56 Resin . . . . .	19
	A. Chain Termination Studies . . . . .	19
	B. Chlorination Studies . . . . .	22
	C. Re-precipitation Studies of the Polymer from Sulfuric Acid . . . . .	23
	Optically Anisotropic Dope Studies . . . . .	24
	A. The AF-R-56 Polymer and Its Chlorinated Derivative . . . . .	27
	B. Other Polymers . . . . .	28
	1. Polybenzimidazoles . . . . .	29
	2. Polyimides . . . . .	30
	3. Polyazomethines . . . . .	32
III	EXPERIMENTAL . . . . .	34
IV	REFERENCES . . . . .	38

## LIST OF ILLUSTRATIONS

<u>Figure</u>		<u>Page</u>
1	The Variation of Brookfield Viscosities of AF-R-56 in Formic Acid/ <u>m</u> -Cresol with Spindle Speed . . . . .	6
2	The Relationship Between Bubble Viscometry and Temperature on AF-Y-56/Formic Acid- <u>m</u> -Cresol Solutions . .	8
3	Final Draw Temperature vs. Percent Tenacity Increase . .	17
4	"Stair-Step" Self-Correcting Conformation for Poly( <u>p</u> -benzamide) . . . . .	25
5	"Alternating" Self-Correcting Conformation for Poly( <u>p</u> -benzamide) . . . . .	25
6	Viscosity as a Function of Concentration for Poly( <u>p</u> -benzamide) in Hydrogen Fluoride at 0°C . . . . .	26
7	Geometry of AF-R-56 Mer Unit . . . . .	27
8	AF-R-56 Polymer in "Straight Rod" Conformation . . . . .	27
9	Possible Hydrogen Bonding to Form Self-Corrected Structure in Formic Acid . . . . .	28
10	Chain Segment of Poly(2,2'- <u>p</u> -phenylene-5,5'-bis-berzimidazole) Showing Straight Rod Conformation . . . .	29
11	Poly(N,N'-ethylene pyromellitic diimide) . . . . .	31
12	Poly[N,N'-(4,4'-azodiphenylene)pyromellitic diimide . . .	31
13	Structure of Polyazoimide Molecule Produced by Bach and Hinderer . . . . .	32



## LIST OF TABLES

<u>Table</u>	<u>Page</u>
I AF-R-56 Dope Dissolution Parameters . . . . .	4
II Brookfield Viscosities of AF-R-56 . . . . .	5
III Variables Associated with the AF-Y-56 Yarn Production . .	10
IV SDO Technique Carried Out on AF-Y-56 for Delineation of the Wet Spinning Variables Leading to High Energy Absorption in the Yarn . . . . .	11
V SDO Operation Carried Out on AF-Y-56 Wet Spinning . . . .	12
VI SDO Operation Carried Out on AF-Y-56 Wet Spinning in Terms of Revised Parameters . . . . .	13
VII Spinning SDO Variable Validation Study . . . . .	15
VIII Fiber Test Results for Spinning SDO Variable Validation Study . . . . .	15
IX Heat Treatment Summary of As-spun AF-Y-56 . . . . .	16
X High Temperature Testing of Heat Treated Fiber . . . . .	18
XI Chain Termination Effects in A-B Polymerization in PPA by Benzoic Acid . . . . .	19
XII Large Scale Chain-Terminated Polymerizations . . . . .	20
XIII Solubility Behavior of Low Molecular Weight AF-R-56 Listed in Descending Order . . . . .	21
XIV Chlorination Studies of AF-R-56 Polymer . . . . .	22
XV Inherent Viscosity Decrease of AF-R-56 Polymers Redrown from Sulfuric Acid . . . . .	23

## SECTION I OBJECTIVES AND SUMMARY OF RESULTS

### PROGRAM OBJECTIVES

The primary objective of this program has been the development of fibers and multifilament yarns exhibiting a high level of mechanical properties, high energy absorption and high temperature performance superior to present materials. These fibers are needed for such applications as high temperature decelerators. In addition, nonflammable and nonmelting fibers upon exposure to high thermal fluxes would be most desirable. Target tensile properties were: tenacity/initial modulus = 20 gpd/1300 gpd at a density less than 1.6 g/cm<sup>2</sup> with thermal retention of 50% of room temperature tenacity at 1400°F (1 min) and 75% of same after 250 hours at 750°F. The suitability of the fiber and yarns for carbonization and graphitization has been a secondary, longer range objective.

### SUMMARY OF RESULTS

The AF-R-56\* system can be prepared as a high molecular weight polymer. Although the exact molecular weight is not known, the measured inherent viscosities of 11 to 17 dl/g\*\* in combination with end capping experiments indicate molecular weights in the 100,000 to 300,000 range. Polymers of such inherent viscosity could be consistently obtained during the course of the program.

The polymer is soluble to a limited extent in concentrated mineral acids (96% H<sub>2</sub>SO<sub>4</sub>, 100% H<sub>3</sub>PO<sub>4</sub>) and in formic acid/meta-cresol mixtures. Most spinning work continued to be done from a mixture of 80% formic acid/20% meta-cresol as results from the previous program<sup>(1)</sup> indicated that despite the low solubility (ca. 2%) fibers spun from this solution possessed better mechanical properties than those prepared from polymer dissolved in mineral acid.

Most of the spinning studies done under the auspices of this program were done utilizing a SDO (self-directed optimization) approach towards maximizing the mechanical properties of fibers wet-spun from 80/20 formic acid/m-cresol into ethyl acetate. Prior to the termination of this phase, it was found that the spinneret hole diameter and the spin/stretch ratio appeared to be the only major factors in optimizing the tensile factor ( $TE^{1/2}$ ) of the fiber.

The properties of the strongest as spun yarn produced under the SDO study were:  $T/E/TE^{1/2} = 6.3/30.8/35.0$ . The reason work was curtailed on the SDO study lay with the low solids content attainable for the polymer

---

\* AF-R-56/ Air Force Resin 56 from Poly-2,5(6)benzimidazole.

\*\* Inherent viscosities of these high molecular weight polymers were measured as 0.005% sulfuric acid solutions.

in the formic acid/m-cresol solution. It was decided that efforts could be better invested in searching for a more suitable solvent or solvent mixture for the AF-R-56 system. Once this solvent system was found it was planned to reinitiate the SDO effort.

Chain termination studies of the AF-R-56 were done, both to monitor molecular weight as a function of inherent viscosity, and to find out whether lower molecular weight polymers at higher dope solids would provide yarns with improved properties. This was not the case for most solvents. However, we were able to obtain up to 30% solids solution in 106% sulfuric acid. Spinning studies from a 16.2% solids solution in this solvent produced a golden yellow yarn ( $T/E/TE^{1/2} = 6.2/12/22$ ). Spinning from 100 +% sulfuric acid had, prior to this time, produced brittle, discolored yarns of very poor mechanical properties. Those preliminary spinning studies had obviously been done with polymer which was incompletely ring closed.

Chlorination of the AF-R-56 produced yet another unusual fiber. It was found that under normal chlorination conditions, the equivalent of only one chlorine per every other mer unit was added. Solubility of the resultant polymer was increased markedly in dimethylacetamide (DMAC) containing lithium chloride. Spinning a 9% solids solution in DMAC containing 2% lithium chloride yielded a fiber with the following properties:  $T/E/TE^{1/2} = 3.1/60/24$ .

Investigation was then directed toward determining whether the AF-R-56 could be induced into exhibiting ordered solution behavior. Physical criteria for ordered polymer solutions are documented.<sup>(2)</sup> In addition to demonstrating stir opalescence and depolarizing polarized light, such solutions also show a decrease in viscosity with increasing solids content after a critical concentration is exceeded. None of these features were found for the AF-R-56 or any of its derivatives in any solvent investigated, although its behavior in formic acid/m-cresol above ~2% concentration suggests some stir opalescence.

Attention was also directed toward the synthesis of other linear polymers in an effort to define solution properties with regard to polymer structure. Three major classes of polymers were investigated: polybenzimidazoles, polyimides and polyazomethines. Ordered solutions were not obtained from these polymers in the solvents investigated.

## SECTION II TECHNICAL DISCUSSION

### THE AF-Y-56 SYSTEM\*

A typical preparation of the AF-R-56 system and spinning dope is included in the Experimental Section. These polymers normally had inherent viscosities of 11 to 17 dl/g (0.005%) in concentrated sulfuric acid. Polymers of lower inherent viscosity could be prepared by the use of end-capping groups as discussed below. Efforts on this phase of the program were directed toward optimizing the mechanical properties of the AF-Y-56 through investigation of the spinning solution, wet spinning and heat treatment parameters.

#### A. Spinning Solution Studies

The preferred solvent system for the AF-R-56 system had been found previously to be a mixture of 80% formic acid and 20% m-cresol.<sup>(1)</sup> Consequently, most of the spinning solution studies were done on dopes of that composition. Most of the dopes were intended for the SDO spinning study and their investigation prior to their use was intended mainly as an aid to that study. The calculated and cataloged variables of these dopes are listed in Table I.

Brookfield viscosities of many of these dopes were measured prior to the spinning studies. Table II lists these dopes in descending order of Brookfield viscosity, along with other data believed pertinent to the viscosities found. Examination of this table shows that with four exceptions, they parallel the dope solids content of the solutions. Three of these four exceptions were of solutions prepared to the same solids content using the same polymer (2225-14-A9). This behavior was anomalous as duplication of other dopes led to a near duplication of the Brookfield viscosities of these dopes. The causative factor for this behavior remains unknown.

A plot of representative dopes comparing spindle speeds with viscosities is shown in Figure 1. As can be seen, the dopes all exhibit non-Newtonian behavior, characteristic of polymer solvent systems under varying shear forces. In general, the spinning solutions exhibited a 50% reduction in the Brookfield viscosity readings for a tenfold increase in spindle speed. Dope velocities through the spinneret orifices were estimated to be about an additional tenfold faster than the 20 rpm employed with the number seven spindle. This value was approximated from the calculated peripheral speed of the spindle and our documented extrusion rates of dopes through a 3 mil electrofoil.

---

\* AF-Y-56/Air Force Yarn from Poly-2,5(6)benzimidazole.

TABLE I

## AF-R-56 DOPE DISSOLUTION PARAMETERS

DOPE	Polymer 2225-	Polymer* Inherent Viscosity	% Solids	% Wt. Formic Acid	% Wt. in the Formic Acid	% Wt. m-Cresol	% Wt. in the m-Cresol	Quantity Mixed (g)	Shear Stirrer Tachometer Reading	Time Stirred (hr)	Dissolution Temp (°C)	Storage Temp (°C)
2239-5-A1	26-A10	16.8	2.0	80	0.8	20	0.01	1000	4.8	17.0	1.0	4.0
-5-A2	24-A8	13.6	1.9	80	2.2	20	0.01	1000	10.5	7.0	1.0	4.0
-5-A3	24-A8	13.6	2.0	80	2.2	20	0.01	1000	4.3	35.5	1.0	4.0
-6-A4	14-A9	15.3	1.7	80	4.3	20	0.01	1000	8.0	20.5	1.0	4.0
-6-A5	17-A11	16.5	1.4	80	4.3	20	0.01	1000	6.0	6.0	1.0	4.0
-6-A6	17-A11	16.5	1.0	80	1.6	20	0.01	1000	6.0	10.5	1.0	4.0
-7-A8	14-A9	15.3	1.7	80	1.3	20	0.01	500	4.4	22.0	1.0	4.0
-7-A9	26-A10	16.8	1.5	80	1.3	20	0.01	500	1.9	23.0	1.0	4.0
-7-A19	24-A8	13.6	2.0	80	0.55	20	0.5	500	10.0	15.5	1.0	6.0
-7-A20	14-A9	15.3	1.8	20	1.1	20	0.5	500	6.0	15.5	1.0	6.0
-7-A21	24-A8	13.6	2.0	80	1.1	20	0.5	500	10.0	13.0	1.0	6.0
-7-A24	21-A10	15.5	1.6	80	1.4	20	0.5	500	7.6	8.0	1.0	6.0
-7-A25	26-A10	16.8	1.6	80	1.4	20	0.5	500	3.0	20.5	1.0	6.0
-7-A26	21-A10	15.5	1.7	80	1.4	20	0.5	500	4.4	16.0	1.0	6.0
-7-A27	21-A10	15.5	1.8	80	2.8	20	0.5	500	6.0	4.5	1.0	6.0
-8-A10	24-A8	13.6	1.4	80	1.3	20	0.01	500	7.6	13.0	1.0	4.0
-8-A11	14-A9	15.3	1.7	80	1.3	20	0.01	500	4.4	24.0	1.0	4.0
-9-A15	21-A10	15.5	1.9	80	0.6	20	0.01	500	6.0	21.5	1.0	4.0
-10-A16	26-A10	16.8	2.0	80	0.6	20	0.01	500	4.4	17.0	1.0	4.0
-10-A17	24-A8	13.6	2.0	80	0.6	20	0.01	500	10.0	19.0	1.0	4.0
-10-A18	14-A9	15.3	1.8	80	0.6	20	0.01	500	6.0			
-23-A1	28-A10	15.2	1.0	100	1.3	None	--	500	20.0	8.0	10.0	4.0
-23-A2	28-A10	15.2	1.0	100	1.3	None	--	100	**	4.0	13.0	4.0
-23-A3	26-A10	16.8	1.5	100	0.6	None	--	100	**	***	13.0	4.0

\* 0.005% in H<sub>2</sub>SO<sub>4</sub>

\*\* These dissolutions were conducted using a battery jar and magnetic stirrer, thus no shaft tachometer reading could be measured.

\*\*\* Polymer did not dissolve completely.

TABLE II

## BROOKFIELD VISCOSITIES OF AF-R-56

Dope Preparation Notebook No.	Polymer Notebook No.	Polymer* Inherent Viscosity	% Solids	Stirrer Shaft Tachometer Reading During Dope	Brookfield, cps x 1000			
					2 RPM	4 RPM	10 RPM	20 RPM
2239-7-A8	2225-14-A9	15.3	1.7	4.4	364	282	184	122
-10-A16	-26-A10	16.8	2.0	4.4	346	275	183	123
-5-A1	-26-A10	16.8	2.0	4.8	290	236	154	105.6
-5-A3	-24-A8	13.6	2.0	4.3	268	210	135	93.4
-8-A11	-14-A9	15.3	1.7	4.4	240	196	132	81
-9-A15	-21-A10	15.5	1.9	6.0	196	170	127	93
-5-A2	-24-A8	13.6	1.9	10.5	190	163	118	83.4
-9-A14**	-28-A10	15.2	1.8	6.0	166	--	104	--
-6-A5	-17-A11	16.5	1.4	6.0	136	114	97	54.4
-6-A4**	-14-A9	15.3	1.7	8.0	110	94	69	50.6
-7-A9	-26-A10	16.8	1.5	1.9	92	76	60	46
-8-A10	-24-A8	13.6	1.4	7.6	80	68	44	41
-8-A12**	-17-A11	16.5	1.0	6.0	44	--	29	--
-6-A6 **	-17-A11	16.5	1.0	6.0	44	37	28	21.5

\* 0.005% in H<sub>2</sub>SO<sub>4</sub>

\*\* Dopes used in bubble viscometry investigation.

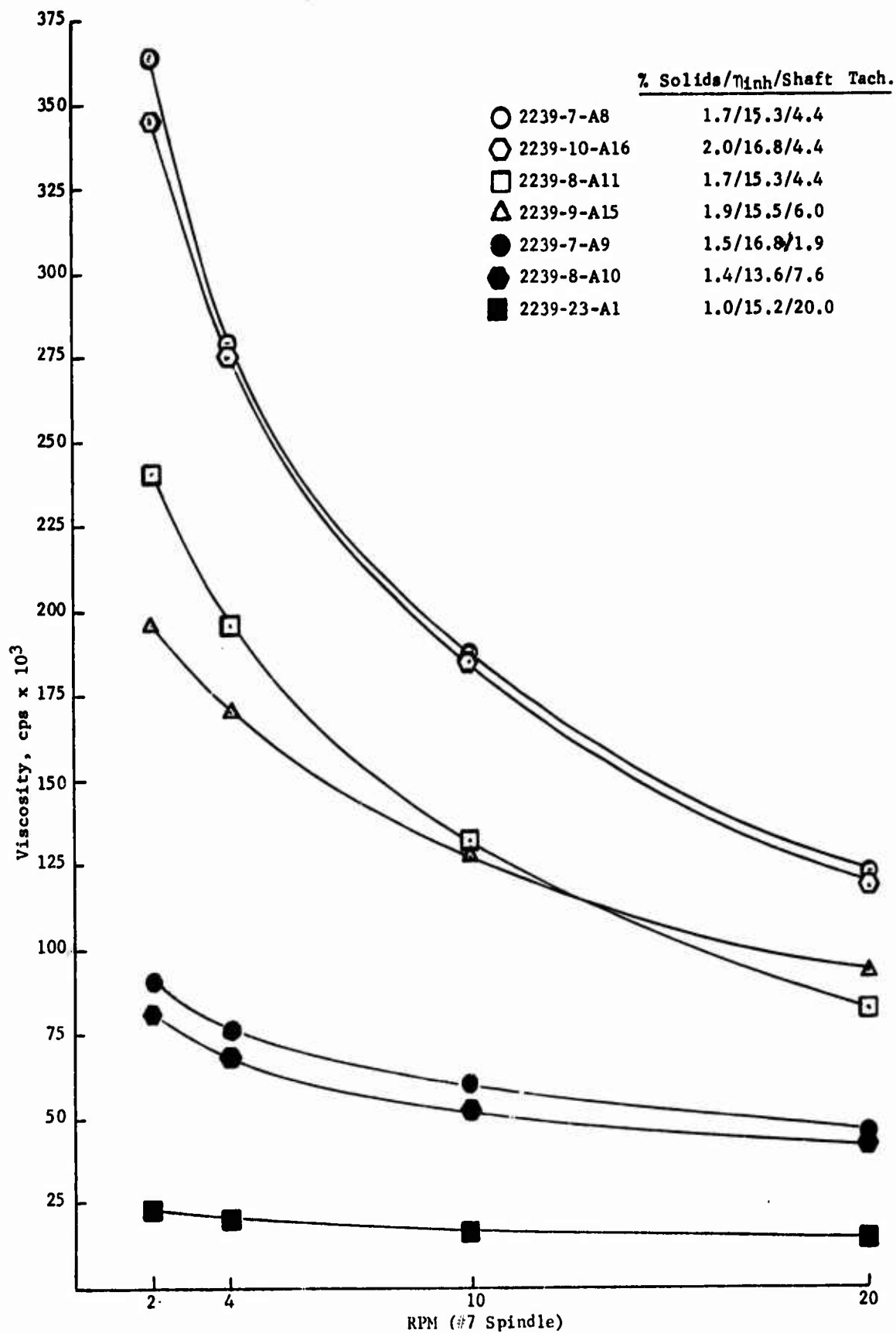


Figure 1. The Variation of Brookfield Viscosities of AF-R-56 in Formic Acid/m-Cresol with Spindle Speed

An attempt was made to characterize the temperature-viscosity behavior of the formic acid/m-cresol/AF-R-56 spinning dopes in order to better understand why there is such a temperature dependence in preparing and storing these solutions as well as to investigate the possibility of spinning at higher temperatures. Samples of four dopes prepared for the SDO wet spinning measurements (Table II) were utilized for this survey. A bubble viscometry method was employed because the volatility and corrosive nature of both the m-cresol and the formic acid preclude heating these dopes in the open. Thus, sealed vials filled with spinning solution, with the exception of a small air space, were placed in a series of constant temperature baths and suddenly inverted. The time interval it took for the air pocket to make its way through the solution is taken to be proportional to the viscosity of the solution. Figure 2 diagrams the results obtained.

The behavior of the dopes in this test is summarized below.

- (a) All of the dopes become cloudy at elevated temperatures indicated in the figure by an arrow.
- (b) All of the solutions reduce in viscosity (logarithmic dependence) with increasing temperature.
- (c) The polymer loses true solubility in the solvent pair at elevated temperatures and the bubble fails to rise upon inversion of the tube due to the very viscous nature of the suspension.
- (d) All of the dopes returned to their original state (clear and same bubble rise time) after being held in an ice bath overnight.
- (e) The dope viscosities (slow → fast bubble rise times) are, as expected, related to the viscosities as determined by the Brookfield viscometer.

The cloud point and desolvation of the polymer do not appear to vary in a regular manner with any of the variables measured in their preparation. Higher solids content dopes do appear, however, to give rise to desolvation at lower temperatures than lower solids dopes.

The behavior of the dopes suggests a delicate balance of solubility for the polymer — at least in this particular ratio of formic acid/m-cresol. For the solvent pair in this ratio, there appears little latitude available to investigate dope temperatures for wet spinning except with low solids spinning solutions.

Table I lists, in addition to the 80/20 formic acid/m-cresol dopes, three spinning solutions prepared with 100% formic acid. The first two, dopes 2239-23-A1 and -A2, prepared at a designed 1.0% solids level, resulted in clear pale yellow solutions, whereas the third spinning solution (2239-23-A3), designed for a 1.5% solids level, did not achieve



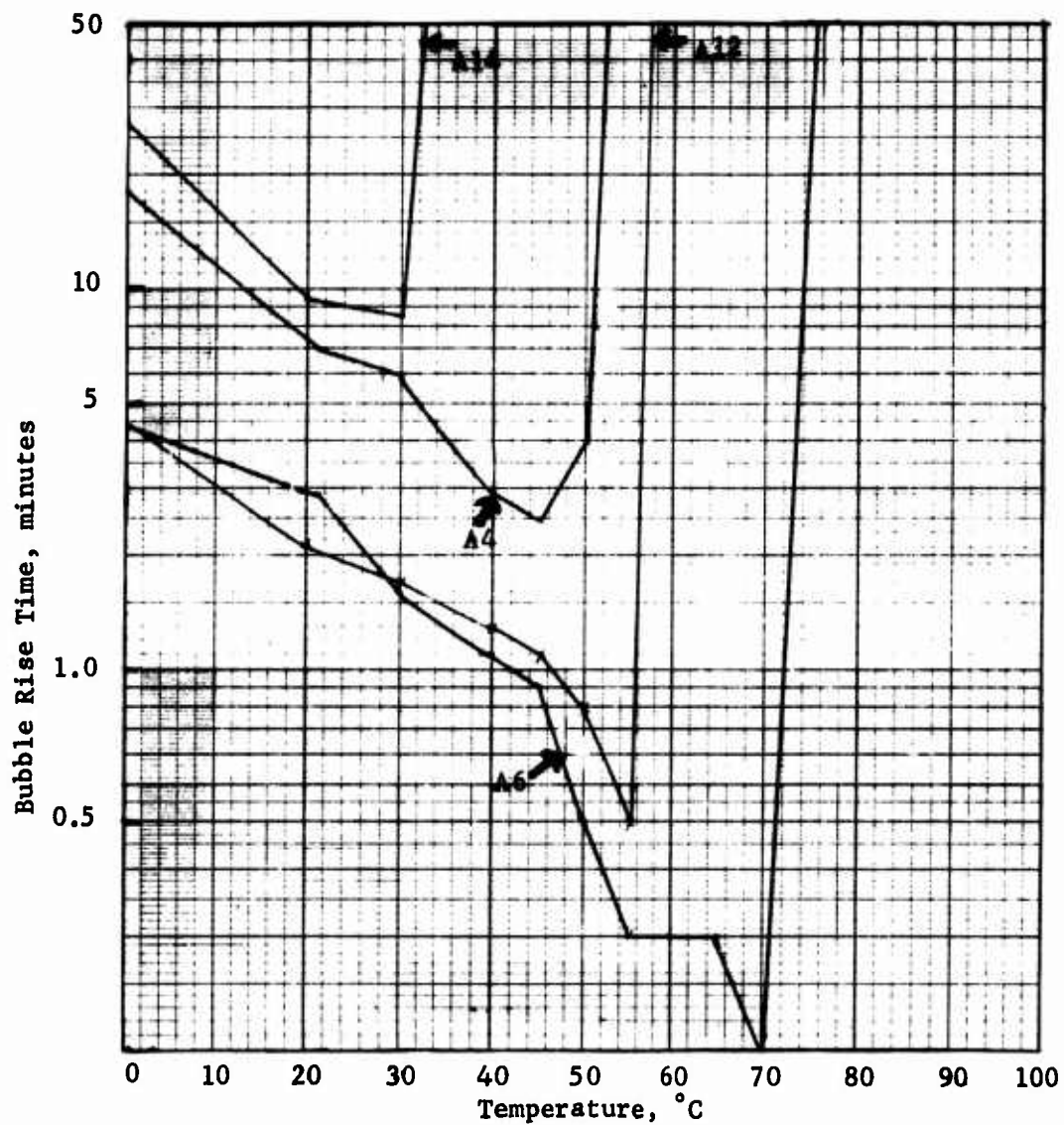


Figure 2. The Relationship Between Bubble Viscometry and Temperature on AF-Y-56/Formic Acid-m-Cresol Solutions

total dissolution. The attainment of these solutions, which appear to be stable for a considerable period of time, even at room temperature, is the reverse of previous observations which indicated that temporary dissolution is obtained but solubility lost after a few hours at room temperature.

#### B. SDO Wet Spinning Studies on Optimization of Fiber Properties

SDO (self-directed optimization) studies of AF-Y-56 properties were initiated under this contract to optimize parameters needed to consistently produce high energy absorption yarns from the AF-R-56. Variables at the time believed associated with the pertinent processes needed to produce this yarn are listed in Table III. The SDO study was conducted with the wet spinning process which was, at that time, defined by 16 variables. The spinning unit itself has been described previously.<sup>(1)</sup>

As some of the variables were considered of only minor importance, a "super saturated" plan was used in which only 12 initial experiments were run instead of the 17 ( $k + 1$ ) experiments deemed necessary in a full scale approach. In accord with this plan, no special sets of conditions were investigated other than those necessary to produce a reasonable threadline. Ranking was based on the tensile factor ( $TE^{1/2}$ ) of the as-spun yarn. The results are listed in Table IV. The next move was decided by the dictum of "twice the average of the best, minus the worst". Thus, as Table IV indicates, the best eight were totaled, averaged and twice this average computed. The parameters of the worst were then individually subtracted from the averages to obtain the parameters by which the next four experiments were to be run. In this manner, additional experiments were conducted and the optimization advanced.

A total of 32 separate experiments were conducted before the program was terminated. Table V contains the data from these results in terms of the initial parameters ranked according to the tensile factor. The most striking interdependence between any of these variables and the tensile factor is found in the spinneret hole diameter (Column 3). Virtually all yarns produced from spinneret orifices smaller than 1.5 mm and larger than 5.0 mm diameter were found to possess low tensile factors.

Table VI summarizes the results in terms of more meaningful variables (function of the variables presented in Table V). No longer is the spinneret hole diameter seen as the predominate in influencing the tensile factor. Apparently playing a major factor is the spin/stretch ratio. In addition, there appears to be indication of consistent variations with bath time. These data indicate some very positive trends, however, as previously mentioned, serious doubt existed as to attainment of the program goals with such low solids content dopes.

TABLE III

VARIABLES ASSOCIATED WITH THE AF-Y-56 PRODUCTION

1. Spinning Dope
  - a. % Wt. formic acid
  - b. % Wt. m-cresol
  - c. % Water formic acid
  - d. % Water m-cresol
  - e. Volume mixed (batch size)
  - f. Shear stirrer, rpm
  - g. Time stirred for dissolution
  - h. Temperature during dissolution
  - i. Temperature of stored dope
  - j. Duration dope stored prior to use
2. Wet Spinning (1st SDO Study)
  - a. Spinneret hole diameter
  - b. Holes/linear inch
  - c. Extrusion area diameter
  - d. Extrusion rate
  - e. Dope % solids
  - f. Dope viscosity (Brookfield)
  - g. Dope, % water
  - h. Bath Length L
  - i. Take up rate
  - j. Dope temperature
  - k. Bath temperature
  - l. Polymer ( $\eta_{inh}$ )
  - m. Relative humidity
  - n. Hours from spinning to workup
  - o. Time spun yarn in oven
  - p. Temperature of oven
3. Hot Drawing
  - a. Length of hot zone
  - b. Time of hot zone exposure (speed)
  - c. Temperature of hot zone
  - d. Draw ratio
  - e. Pass multiplicity (obviously if multiple passes are required, then a  $\rightarrow$  d will become a series of multiple sub-routines)

TABLE IV

SDO TECHNIQUE CARRIED OUT ON AF-Y-56 FOR DELINEATION OF THE  
WET SPINNING VARIABLES LEADING TO HIGH ENERGY ABSORPTION IN THE YARN  
(12 Experiments Completed, A-13, A-14, A-15, A-16 Scheduled Next)

Exper. No.	Splinteret Hole Diameter, mils	# Holes per Linear Inch of Electrofoil	Splinteret Area Diameter, mm	Dope Extrusion Rate, g/min	Dope % Solids	Shalt, Reading	% H <sub>2</sub> O in Dope	Bath Length, cm	Take-up Rate, Tachometer Reading	Dope Temp, °C	Bath Temp, °C	Polymer Vinh, dl/g	Relative Humidity, %	Time from Spin to Work-up, hr	Time in Oven, hr	Oven Temp, °C	Rank	TF 1/2	Tenacity, Rpd
A1	3	100	6.0	5.39	2.0	4.8		198	6.6	8	22	16.8	60	3.0	1.0	150	1	28.9	4.6
A3	3	100	8.0	5.38	1.9	10.5		185	5.2	4	18	13.6	70	1.0	1.0	150	2	28.9	4.7
A12	3	100	8.0	3.40	1.4	6.0		210	8.0	7	13	16.5	60	1.5	1.0	170	3	27.6	5.3
A5	3	100	10.0	6.95	2.0	4.3		210	4.0	2	11	13.6	65	1.5	1.0	150	4	26.0	5.4
A10	3	100	8.0	3.84	1.4	6.0		210	8.0	4	19	16.5	60	0.5	1.0	175	5	24.3	5.3
A6	3	100	8.0	5.66	2.0	4.3		210	4.0	2	11	13.6	64	1.75	1.5	150	6	21.6	4.2
A7	5	30	10.0	3.25	1.7	8.0		190	7.0	5	33	15.3	71	64.5	0.5	110	7	18.8	2.7
A11	7.5	40	8.0	3.14	1.4	6.0		210	8.0	4	19	16.5	71	19.0	1.5	170	8	17.3	4.4
8 Best Total Average	30.5	670	66.0	37.01	13.5	44.9		1623	50.8	37	147	122.4	521	92.75	8.5	1225			
Twice Average	3.8	84	8.25	4.63	1.7	6.2		203	6.4	5	18	15.3	65	11.6	1.0	153			
Twice Average	7.6	168	16.50	9.26	3.4	12.4		405	12.8	10	36	30.6	130	23.2	2.0	306			
Twice Average	7.6	168	16.50	9.26	3.4	12.4		406	12.8	10	36	30.6	130	23.2	2.0	306			
A9	7.5	40	8.0	5.84	1.7	8.0		210	4.5	5	21	15.3		16.75	4.0	110	9	15.7	3.0
A13	.1*	128	8.5	3.42	1.7	4.4		196	8.3	5	15	15.3	77	6.5	(-2.0)*	176			
Twice Average	7.6	168	16.50	9.26	3.4	12.4		406	12.8	10	36	30.6	130	23.2	2.0	306			
A2	3.0	100	8.0	5.59	1.9	10.5		191	6.2	7	18	13.6	65	17.75	1.0	150	10	14.7	3.4
A14	4.6	68	8.5	3.67	1.5	1.9**		215	6.6	3	18	17.0	65	5.45	1.0	156			
Twice Average	7.6	168	16.50	9.26	3.4	12.4		406	12.8	10	36	30.6	130	23.2	2.0	306			
A8	3.0	100	10.0	14.62	1.7	8.0		210	8.0	5	21	15.3	53	3.0	1.0	110	11	14.0	3.0
A15	4.6	68	6.50	(-5.38)*	1.7	4.4		196	4.8	5	15	15.3	77	20.2	1.0	196			
Twice Average	7.6	168	16.50	9.26	3.4	12.4		406	12.8	10	36	30.6	130	23.2	2.0	306			
A4	13	150	8.0	2.09	2.0	4.8		100	8.0	5	12	16.8	69	15.0	2.0	150	12	5.65	2.5
A16	(-5.4)*	153	8.5	7.17	1.4	7.6		306	4.8	5	24	13.8	61	8.2	0.0	156			

\* Experimentally inaccessible

\*\* Experimentally possible but with difficulty

TABLE V

SDO OPERATION CARRIED OUT ON AF-Y-56 WET SPINNING  
(32 Completed Experiments Ranked in Order at Decreasing Tensile Factor)

Rank	Exper. No.	Splinteret Hole Diameter (mils)	No. Holes Per Linear Inch of Electrofoil	Splinteret Area (mm)	Dope Extrusion Rate (g/min)	Dope % Solids	Shaft Tachometer Reading	% H <sub>2</sub> O in Dope	Bath Length (cm)	Takeup Rate Tachometer Reading	Dope Temp (°C)	Bath Temp (°C)	Polymer Msh (dl/g)	Relative Humidity (%)	Time from Spin to Workup (hr)	Time in Oven (hr)	Oven Temp (°C)	$\tau_{1/2}$	Tenacity (Gpd)
1	A23	3.0	100	8.0	3.33	1.7	4.4		196	8.3	5.0	17.0	15.5	47	9.5	1.0	150	35.0	6.3
2	A29	2.4	125	10.0	8.72	1.6	8.4		187	8.2	6.2	21.2	15.9	42	49.8	1.0	108	32.0	5.3
3	A25	3.0	100	8.0	3.24	1.4	7.7		161	7.2	8.0	24.0	16.8	46	22.5	1.0	173	30.3	6.2
4	A30	2.4	80	8.0	4.02	1.3	8.5		173	9.0	9.2	23.6	17.6	39	13.5	1.0	154	28.9	6.0
5	A3	3.0	100	8.0	5.38	1.9	10.5		185	5.2	4.0	18.0	13.6	70	1.0	1.0	150	28.9	4.7
6	A1	3.0	100	6.0	5.39	2.0	4.8		198	6.6	8.0	22.0	16.8	60	3.0	1.0	150	28.9	4.6
7	A12	3.0	100	8.0	3.40	1.4	6.0		210	8.0	7.0	13.0	16.5	60	1.5	1.0	170	27.6	5.3
8	A21	1.5	125	8.0	7.04	1.6	7.6		163	4.8	6.5	25.0	15.5	53	22.0	1.0	150	26.3	4.0
9	A5	3.0	100	10.0	6.95	2.0	4.3		210	4.0	2.0	11.0	13.6	65	1.5	1.0	150	26.0	5.4
10	A10	3.0	100	8.0	3.84	1.4	6.0		210	8.0	4.0	19.0	16.5	60	0.5	1.0	175	24.3	5.3
11	A6	3.0	100	8.0	5.66	2.0	4.3		210	4.0	2.0	11.0	13.6	64	1.75	1.5	150	21.6	4.2
12	A15	3.0	100	6.0	0.89	1.7	4.4		196	4.8	5.0	16.0	15.3	61	65.0	1.0	196	21.6	3.9
13	A7	5.0	30	10.0	3.25	1.7	8.0		190	7.0	5.0	33.0	15.3	71	64.5	0.5	110	18.8	2.7
14	A11	7.5	40	8.0	3.14	1.4	6.0		210	8.0	4.0	19.0	16.5	71	19.0	1.5	170	17.3	4.4
15	A9	7.5	40	8.0	5.84	1.7	8.0		210	4.5	5.0	21.0	15.3	--	16.75	4.0	110	15.7	3.0
16	A13	3.0	30	8.5	3.41	1.7	4.4		196	8.3	3.5	16.0	15.3	57	6.5	0.0	--	15.2	1.8
17	A2	3.0	100	8.0	5.59	1.9	10.5		191	6.2	7.0	18.0	13.6	65	17.75	1.0	150	14.7	3.4
18	A19	5.0	30	8.0	1.70	2.0	4.4		139	7.0	5.0	11.0	16.8	66	26.4	2.0	287	14.4	4.4
19	A8	3.0	100	10.0	14.62	1.7	8.0		210	8.0	5.0	21.0	15.3	53	3.0	1.0	110	14.0	3.0
20	A14	5.0	30	8.5	3.60	1.5	2.0		215	6.6	4.5	20.0	16.8	65	5.5	1.0	156	12.7	2.7
21	A20	1.5	125	8.0	5.08	2.0	10.0		187	5.2	5.0	16.0	13.6	61	29.1	1.0	156	12.6	3.8
22	A18	3.0	100	8.0	5.26	1.9	7.6		206	3.5	6.0	20.0	15.5	69	28.1	1.0	287	11.8	4.2
23	A31	0.78	125	6.0	6.44	1.6	4.8		193	3.8	6.0	4.0	15.5	60	2.5	2.0	194	8.2	3.5
24	A17	0.78	125	8.0	5.54	1.8	6.0		192	3.8	6.0	17.0	15.3	55	15.6	0.5	142	7.6	2.9
25	A24	5.0	30	8.0	3.06	1.8	6.0		210	8.0	2.0	19.0	15.5	74	16.6	1.5	169	7.4	3.0
26	A16	0.78	125	8.5	6.98	1.4	7.6		263	4.8	4.5	25.0	13.6	60	8.2	0.0	--	7.0	0.6
27	A22	5.0	30	8.0	3.88	1.6	2.0		215	6.6	5.0	20.0	16.8	76	6.3	1.0	157	6.1	2.5
28	A28	0.78	125	8.0	5.23	1.8	10.0		156	4.6	5.0	15.0	13.6	75	22.0	1.0	167	6.1	2.7
29	A4	13.0	15	8.0	2.09	2.0	4.8		100	8.0	5.0	12.0	16.8	69	15.0	2.0	150	5.7	2.5
30	A27	0.78	125	8.0	5.88	1.6	6.0		161	3.2	5.0	16.0	15.5	77	9.7	0.5	153	4.8	2.1
31	A32	0.78	125	8.0	6.76	1.9	6.8		173	5.0	7.0	18.0	15.5	40	1.0	1.0	136	4.7	2.0
32	A26	0.78	125	6.0	5.75	1.7	4.0		181	3.2	5.0	2.0	15.5	48	1.0	1.5	213	1.5	1.1

TABLE VI

SDO OPERATION CARRIED OUT ON AF-Y-56 WET SPINNING IN TERMS OF REVISED PARAMETERS

Rank	Expt. No.	Spinneret Hole Diameter (mm)	No. Holes Per Linear Inch of Electrofoil	Extrusion Area	Dope Extrusion Rate (g/min)	Dope % Solids	Dope Temp (°C)	Bath Temp (°C)	Polymer Visc (dl/g)	Spinn Stretch $V_2/V_1$	Bath Time (min)	Bath Solvent	Dope Constituents 80% HCOOH 20% m-Cresol	Calc. % H <sub>2</sub> O in Dope	Time from Spinn to Workup (hr)	Time in Oven (hr)	Oven Temp (°C)	$t_g^{1/2}$	Tenacity (gpd)
1	A23	3.0	100	8.0	3.33	1.7	5.0	17.0	15.5	3.63	0.99	EtOAc		1.2	9.5	1.0	150	35.0	6.3
2	A29	2.4	125	10.0	8.72	1.6	6.2	21.2	15.9	2.27	0.84			1.0	49.8	1.0	108	32.0	5.3
3	A25	3.0	100	8.0	3.24	1.4	8.0	24.0	16.8	3.24	0.91			0.9	22.5	1.0	173	30.3	6.2
4	A30	2.4	80	8.0	4.02	1.3	9.2	23.6	17.6	1.42	0.60			1.3	13.5	1.0	159	28.9	6.0
5	A3	3.0	100	8.0	5.38	1.9	4.0	18.0	13.6	1.08	0.98			1.8	1.0	1.0	150	28.9	4.7
6	A1	3.0	100	6.0	5.39	2.0	8.0	22.0	16.8	1.00	0.80			0.7	3.0	1.0	150	28.9	4.6
7	A12	3.0	100	8.0	3.40	1.4	7.0	13.0	16.5	3.43	1.08			3.5	1.5	1.0	170	27.6	5.3
8	A21	1.5	125	8.0	7.04	1.6	6.5	25.0	15.5	0.65	0.71			1.2	22.0	1.0	150	26.3	4.0
9	A5	3.0	100	10.0	6.95	2.0	2.0	11.0	13.6	1.31	1.59			1.8	1.5	1.0	150	26.0	5.4
10	A10	3.0	100	8.0	3.84	1.4	4.0	19.0	16.5	3.04	1.05			3.5	0.5	1.0	175	24.3	5.3
11	A6	3.0	100	8.0	5.66	2.0	2.0	11.0	13.6	1.03	1.42			1.8	1.75	1.5	150	21.6	4.2
12	A15	3.0	100	6.0	0.89	1.7	5.0	16.0	15.3	3.07	1.64			1.1	65.0	1.0	196	21.6	3.9
13	A7	5.0	30	10.0	3.25	1.7	5.0	33.0	15.3	1.28	0.81			3.6	64.5	0.5	110	18.8	2.7
14	A11	7.5	40	8.0	3.14	1.4	4.0	19.0	16.5	3.90	1.11			3.5	19.0	1.5	170	17.3	4.4
15	A9	7.5	40	8.0	5.84	1.7	5.0	21.0	15.3	1.18	1.35			3.5	16.75	4.0	110	15.7	3.0
16	A13	3.0	30	8.5	3.41	1.7	3.5	16.0	15.3	0.36	0.33			1.1	6.5	0.0	--	15.2	1.8
17	A2	3.0	100	8.0	5.59	1.9	7.0	18.0	13.6	0.79	1.49			1.8	17.75	1.0	150	14.7	3.4
18	A19	5.0	30	8.0	1.70	2.0	5.1	11.0	16.8	1.61	0.65			0.5	26.4	2.0	287	14.4	4.4
19	A8	3.0	100	10.0	14.62	1.7	5	21.0	15.3	1.24	0.78			3.5	3.0	1.0	110	14.0	3.0
20	A14	5.0	30	8.5	3.60	1.5	4.5	20.0	16.8	0.79	0.77			1.0	5.5	1.0	156	12.7	2.7
21	A20	1.5	125	8.0	5.08	2.0	5.0	16.0	13.6	0.52	0.65			1.0	29.1	1.0	156	12.6	3.8
22	A18	3.0	100	8.0	5.26	1.9	6.0	20.0	15.5	0.97	1.55			0.5	28.1	2.0	287	11.8	4.2
23	A31	0.78	125	6.0	6.44	1.6	6.0	4.0	15.5	0.08	0.13			1.3	2.5	2.0	194	8.2	3.5
24	A17	0.78	125	8.0	5.54	1.8	6.0	17.0	15.3	0.19	0.25			1.0	15.6	0.5	142	7.6	2.9
25	A24	5.0	30	8.0	3.06	1.8	2.0	19.0	15.5	0.98	0.69			2.4	16.6	1.5	169	7.4	3.0
26	A16	0.78	125	8.5	6.98	1.4	4.5	25.0	13.6	0.13	0.33			1.1	8.2	0.0	--	7.0	0.6
27	A22	5.0	30	8.0	3.88	1.6	5.0	20.0	16.8	0.67	0.70			1.2	6.3	1.0	157	6.1	2.5
28	A28	0.78	125	8.0	5.23	1.8	5.0	15.0	13.6	0.14	0.23			1.0	22.0	1.0	167	6.1	2.7
29	A4	13.0	15	8.0	2.09	2.0	5.0	12.0	16.8	1.79	0.43			0.7	15.0	2.0	150	5.7	2.5
30	A27	0.78	125	8.0	5.88	1.6	5.0	16.0	15.5	0.09	0.72			1.0	9.7	0.5	153	4.8	2.1
31	A32	0.78	125	8.0	6.76	1.9	7.0	18.0	15.5	0.12	0.70			1.3	1.0	1.0	136	4.7	2.0
32	A26	0.78	125	6.0	5.75	1.7	5.0	2.0	15.5	0.05	0.15			1.0	1.0	1.5	213	1.5	1.1

Finally, a validation study was run on the SDO method in order to determine whether all of the key variables had been included in these spinning studies. Three additional wet spinning studies were carried out using almost identical parameters. These variables are listed in Table VII. Their selection was again arbitrarily determined to afford ease in spinning and reasonable certainty of maintaining a threadline. The results indicate that the key spinning variables have indeed been included. Table VIII indicates the actual test values for eleven specimens and their average and standard deviation.

### C. Heat Stretching and Fiber Studies

Emphasis on heat treating studies centered upon finding the right set of parameters (listed in Table III) to give the optimum mechanical properties for the AF-Y-56. Attempts were made to determine the actual temperature the yarn is exposed to during the heat treating process.

Yarn properties developed with heat treating the AF-Y-56 are summarized in Table IX. It can be seen from the table that the highest tenacity level obtained was achieved ( $T/E/Mi/TE^{1/2} = 10.6/2.0/551/15.1$ ) by a single pass at a furnace temperature of 600°C. The improvement between percent tenacity increase experienced from the as-spun state to the hot stretched state gave the result plotted in Figure 3. Clearly suggested is the investigation of higher temperatures than 600°C and/or multiple draws at ~600°C for possible tenacity increases. It had been decided that once the SDO method for wet spinning had developed a program that would give tenacity levels of 8 g/den or greater for as-spun fibers, an SDO heat stretching program would be initiated.

Seven of the heat treated fibers listed in Table IX were selected for moisture regain studies. The data shows a slight trend for decreasing percent moisture regain with increasing final pass temperature, the values ranging from 28% at the 400°C final pass temperature to ca. 23% at the 600°C final pass temperature.

In conjunction with the heat treatment studies, fiber testing at elevated temperature was also initiated. All of the tests were with 10-inch gauge lengths (9 inches subjected to the hot zone). The fibers experienced a one minute soak at temperature in air prior to testing. Table X summarizes the data. Examination of the table reveals that percent retention of room temperature tenacity is ca. 75-80% at 600°F and 46% at 750°F. Extrapolation of this retention data shows that if an 18 gpd fiber could be produced, it should have at least 8 gpd at 750°F (400°C).

TABLE VII

SPINNING SDO VARIABLE VALIDATION STUDY  
[Same dope (6-A6) used in three separate spins]

Exper. No.	Spinneret Hole Dia. mm	No. Holes per inch	Extrusion Area Dia. mm	Extrusion Rate, g/min	Dope % Solids	Shaft Tachometer	Dope % H <sub>2</sub> O	Bath Length cm	Take Up Rate Tachometer Reading	Dope Temp °C	Bath Temp °C	Polymer $\eta_{inh}$	Relative Humidity %	Time from Spin to Workup, hr	Time in Oven, hr	Oven Temp °C
2239-45-A1	3.0	100	8.0	3.51	1.0	4.0		210	4.0	8.0	21.0	16.5	56.5	16.8	1.0	126
-45-A2	3.0	100	8.0	3.47	1.0	4.0		210	4.0	8.0	21.0	16.5	64.0	16.8	1.0	126
-45-A3	3.0	100	8.0	3.55	1.0	4.0		210	4.0	8.0	21.0	16.5	62.0	16.8	1.0	126

TABLE VIII

YARN TEST RESULTS FOR SPINNING SDO  
VARIABLE VALIDATION STUDY

Exper. No.	Elongation (%)	Tenacity (gpd)	Modulus (gpd)	TE <sup>1/2</sup>
2239-45-A1	47.8	4.34	105.0	30.01
	50.0	4.13	80.5	29.20
	46.2	4.15	73.5	28.19
2239-45-A2	48.8	4.38	83.6	30.58
	64.8	4.22	73.6	33.95
	59.2	4.08	71.6	31.38
	53.5	4.08	73.6	29.83
2239-45-A3	59.2	4.30	78.1	33.06
	57.5	3.98	76.3	30.18
	52.5	3.92	76.3	28.43
	58.0	3.92	74.4	29.89
Average	54.3	4.14	78.78	30.43
Standard Deviation	5.85	0.161	9.374	1.779



TABLE IX

## HEAT TREATMENT SUMMARY OF AS-SPUN AF-Y-56

HEAT TREATED FIBER														
Yarn Code	Parent Yarn	Denier (Dry)	Tenacity	Elongation	M <sub>i</sub>	TE <sup>1/2</sup>	Max Temp	Denier (Dry)	Tenacity	Elongation	M <sub>i</sub>	TE <sup>1/2</sup>	% Tenacity Increase	% Moisture Regain
2232-40-A9	2232-13-A6	331.5	4.9	19.0	107.4	21.4	600	225.0	9.8	2.2	509	14.3	99	22.3
-40-B1							400	255.6	9.0	2.7	390	14.6	83	--
-40-B2							500	228.6	8.7	1.8	499	11.8	78	26.1
-40-B3							400	229.5	8.0	1.7	501	10.3	63	27.8
-41-B4							600	246.3	9.5	2.4	445	14.7	93	23.6
-41-B5							600	237.9	9.9	2.1	508	14.5	102	21.1
-41-B6A							500	234.4	7.9	2.2	416	11.5	60	25.4
-41-B6B							600	226.3	10.6	2.0	551	15.1	117	24.3
-41-B7A							300	306.4	4.9	3.9	185	9.7	2	--
-41-B7B							400	256.0	6.1	1.8	351	8.1	24	--
-42-C1A	2232-13-A7	349.8	4.3	26.2	91.0	22.1	600*	272.9	9.7	3.9	341	19.0	124	--
-42-C1B							700*	243.0	10.1	4.1	443	20.4	134	--
-42-C3	2232-14-B3	300.0	4.4	35.7	92.2	26.4	600*	178.0	8.2	1.4	545	9.7	85	--
-42-C4							600	187.9	7.6	1.8	476	10.1	72	--

\* One inch gauge lengths

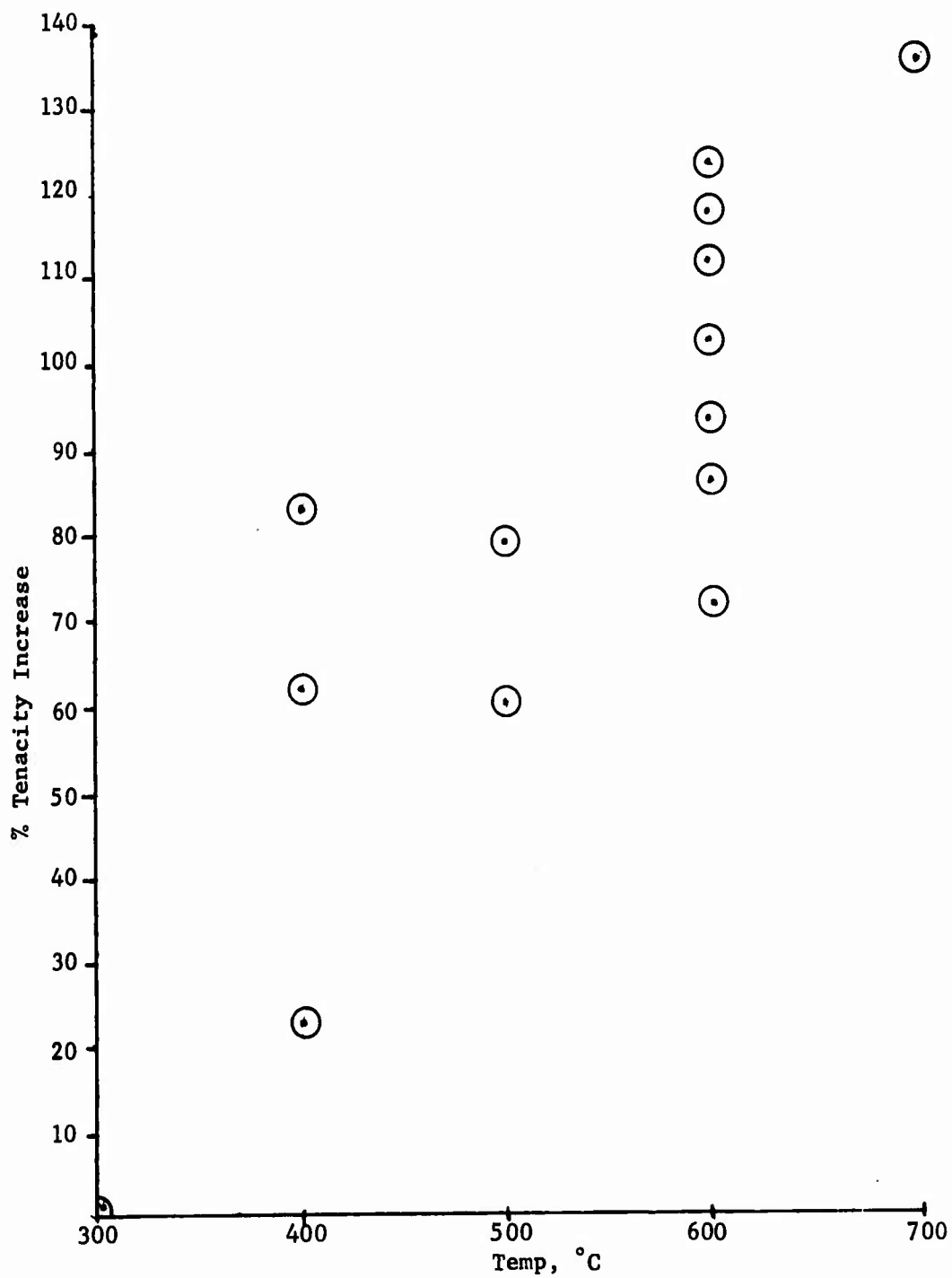


Figure 3. Final Draw Temperature vs. % Tenacity Increase

TABLE X  
HIGH TEMPERATURE TESTING OF HEAT TREATED YARN

<u>Fiber</u>		<u>Test Temp</u>	<u>Tenacity (g/den)</u>	<u>Elong. (%)</u>	<u>M<sub>1</sub> (g/den)</u>	<u>TE<sup>1/2</sup></u>	<u>% Ten. Retent.</u>
<u>As Spun</u> 2232-13-A6		RT	4.9	19.0	107	21.4	--
<u>Heat Treated</u>							
400°C Final Pass	{ 2232-40-B3	RT	8.0	1.7	501	10.3	
		600°F	6.0	2.0	351	8.4	75
	{ 2232-41-B7B	RT	6.1	1.8	352	8.1	
		750°F	2.8	3.7	146	5.4	46
500°C Final Pass	{ 2232-40-B2	RT	8.7	1.8	499	11.8	
		600°F	6.7	1.8	412	9.1	77
600°C Final Pass	{ 2232-41-B4	RT	8.5	2.4	445	14.7	
		600°F	7.0	3.1	336	12.2	82
	{ 2232-41-B5	RT	9.9	2.1	508	14.5	
		700°F	5.2	2.9	257	8.9	53

## MODIFICATIONS OF THE AF-R-56 RESIN

To maintain molecular alignment required to achieve a high performance fiber from a low solids dope through the coagulation process would intuitively be most difficult. The studies described below were directed toward increasing the solids content of the dopes yet retaining low enough viscosity for spinnability.

### A. Chain Termination Studies

One known way of increasing the solids concentration of the AF-R-56 while maintaining a given viscosity was to decrease the molecular weight of the polymer. This was accomplished by polymerization in the presence of a small, accurately weighed amount of benzoic acid which acted as a chain terminating agent. These experiments performed two functions. They allowed one to determine whether a greater concentration of polymer of a lower inherent viscosity in a particular spinning solution would improve the properties of a fiber wet-spun from that solution. Secondly, they allowed the calculation, at least for polymers of lower molecular weight, of a molecular weight in terms of inherent viscosity.

Chain termination studies had been undertaken on the previous program to accomplish the latter function. These results are shown in Table XI.

TABLE XI  
CHAIN TERMINATION EFFECTS IN A-B POLYMERIZATION  
IN PPA BY BENZOIC ACID

<u>Sample</u>	<u><math>\eta_{inh}^*</math> H<sub>2</sub>SO<sub>4</sub></u>	<u>Calculated D.P.**</u>	<u>Calculated Molecular Weight</u>
Unmodified Control	5.14	High	High
1st $\phi$ CO <sub>2</sub> H Increment	4.10	468	71,000
2nd $\phi$ CO <sub>2</sub> H Increment	2.33	250	29,000
3rd $\phi$ CO <sub>2</sub> H Increment	1.35	114	13,000

\* 0.05% H<sub>2</sub>SO<sub>4</sub>

\*\* Degree of polymerization, assumes 1 mole of benzoic acid added to 100 moles of 3,4-diaminobenzoic acid yields a D.P. = 100.

Subsequently, six additional end-capped polymerizations were conducted. The amount of benzoic acid added to these would theoretically give a calculated D.P. of 258 for each polymer. The inherent viscosities of the six polymers were 2.71, 2.76, 2.92, 3.09, 2.71 and 2.39 (0.5% H<sub>2</sub>SO<sub>4</sub>), respectively. These slightly higher values appear to substantiate the fact that the monomer used previously was of poorer quality. Thus, these inherent viscosities (average of closest five = 2.84) indicate a number average molecular weight of ~30,000.

Two large scale runs were subsequently made. Table XII lists the salient points. The results of these runs compare favorably with those described above.

TABLE XII

LARGE SCALE CHAIN TERMINATED POLYMERIZATIONS

<u>Polymer Batch No.</u>	<u><math>\eta_{inh}</math> (0.5% in H<sub>2</sub>SO<sub>4</sub>)</u>	<u>Calculated D.P.</u>	<u>Calculated Molecular Weight</u>
2239-44-IV A	2.72	250	29,000
2239-38-2	1.82	100	11,600

Solvent studies utilizing chain terminated low inherent viscosity resins are listed in Table XIII. With the exception of trifluoromethane sulfonic acid which had not been previously tried, solubilities of low molecular weight polymers paralleled those of higher molecular weight AF-R-56 resins. Some increase in solubility was noted but, with one exception, this was offset by a lack of improvement in the mechanical properties exhibited by fibers spun from these solutions.

Attempts to spin low molecular weight AF-R-56 from either formic acid or 80/20 formic acid/m-cresol did not lead to maintenance of the threadline. Evidently, the effect of the loss in polymer molecular weight on its fiber characteristics has not been offset by the increase in polymer solubility in these particular solvent systems. More spinning parameters should be investigated, however, to ascertain whether this is a correct conclusion or whether its simply a matter of adjusting the parameters to accommodate the low molecular weight of the resin.

TABLE XIII  
SOLUBILITY BEHAVIOR OF LOW MOLECULAR WEIGHT AF-R-56  
LISTED IN DESCENDING ORDER\*

<u>Solvent</u>	<u>Maximum % Solids</u>	<u>Comments</u>
106.3% H <sub>2</sub> SO <sub>4</sub>	30	Became too thick to stir at this solids level
80:20 formic acid/ <u>m</u> -cresol	4.5	
Formic acid	3.5	Increase to 4% gave gel
Trifluoromethane/ sulfonic acid	>3.0	Quite viscous at 3% solids
KOH/H <sub>2</sub> O	<<2.0	Some dissolved polymer precipitated during subsequent filtration
DMAC·LiCl	~2.0	8% LiCl
NMP	<<1.0	Very little solubility
Chloroacetic acid/ <u>m</u> -cresol	0	Solvents immiscible
Trichloroacetic acid/ <u>m</u> -cresol	0	Solvents immiscible
1-Acetyl pyridine	0	

---

\* DP 250 polymer used in all studies.

In preparing formic acid/m-cresol dopes composed of a mixture of low and high inherent viscosity AF-R-56 resins, we were able to increase the solids content of the solutions over those prepared from high polymer alone. We were also able to maintain a threadline using our standard wet spinning parameters, although the fibers obtained from wet spinning these dopes suffer from very poor mechanical properties. These may be the result of either the low inherent viscosity polymer directly or non-optimized parameters in the wet spinning process to accommodate such a system.

Wet spinning of low inherent viscosity AF-R-56 in 106% sulfuric acid was more successful. As shown in Table XIII the polymer is soluble in 106% sulfuric acid to 30 weight percent. A 16.6% solids 106.3% sulfuric acid solution of the D.P. 250 polymer was spun into distilled water at room temperature. The mechanical properties of the resultant fiber are not outstanding (tenacity = 6.2 g/d, elongation = 12%, tensile factor = 22) when compared to the best obtained for this resin system, but they are both the best achieved for low inherent viscosity AF-R-56 and the best achieved for any AF-R-56 spun from sulfuric acid. A further note of interest is that this yarn was golden yellow in color, indicating that those brittle, discolored AF-Y-56 spun from 100% sulfuric acid under the previous program<sup>(1)</sup> were evidently spun from polymer which was not completely ring closed and thus subject to oxidative attack by the acid.

#### B. Chlorination Studies

Samples of various batches of AF-R-56 were dissolved in sulfuric acid in the presence of iodine and heated to 75°C. Chlorine gas was then bubbled through the solution for approximately 6 hours. About half the available mer units were chlorinated (as shown in Table XIV) with this procedure.

TABLE XIV  
CHLORINATION STUDIES OF AF-R-56 POLYMER

Run No.	$\eta_{inh}$ Starting Polymer	$\eta_{inh}$ Chlorinated Polymer	% Cl*	Chlorine per Mer Unit
1	11.7	6.52	13.0	~ 1/2
2	16.8	6.0	13.10	
3	15.2	8.9	14.8	

\* By analysis, Galbraith Laboratories, Inc., Knoxville, Tenn.

The chlorinated AF-R-56 showed considerable increase in solubility over the unchlorinated AF-R-56. Thus, a sample of the chlorinated AF-R-56 could be dissolved in DMAC containing 6% lithium chloride to the extent of 12%. The polymer also appeared to be soluble in sulfuric acid and formic acid/m-cresol.

Preliminary spinning studies were run on the chlorinated polymer. A 9% solids solution was prepared in DMAC containing 2% lithium chloride as the solvent system. This was spun into a methanol bath at 17°C through a 3.0 mil/100 hole/in. spinneret. The resultant yarn had the following properties: T/E/TEI/2 = 3.1/60/24.

### C. Re-precipitation Studies of the Polymer from Sulfuric Acid

It was decided to dissolve some of the polymer in sulfuric acid and re-precipitate it in order to further purify it.\* These sulfuric acid re-precipitations were found to decrease the inherent viscosity of the polymer, probably by cleaving those remaining uncyclized benzimidazole units on the chain. Table XV indicates the reductions in inherent viscosity observed.

TABLE XV  
INHERENT VISCOSITY DECREASE OF AF-R-56 POLYMERS  
REDROWN FROM SULFURIC ACID

<u>Dope</u>	$\eta_{inh}$ Polymer (dl/g)	$\eta_{inh}$ after <u>Re-precipitation</u>	<u>Comments</u>
2225-3-A10	11.7	8.0	Vacuum dried at RT
2225-19-A8	13.1	10.2	Vacuum dried at RT
2239-44-IV A	2.72	2.02	Dried at 50°C, Trace SO <sub>4</sub>
		1.95	Dried at 150°C, Trace SO <sub>4</sub>
		2.25	Dried at 50°C No SO <sub>4</sub>
		2.16	Dried at 150°C No SO <sub>4</sub>

The resultant re-precipitated polymer did not exhibit the sought tendency to be more capable of ordered solution behavior in the standard solvents than virgin polymers of comparable inherent viscosities.

\* A residual inorganic material or ash was found to comprise up to 0.7% of the polymer weight after workup. The material, principally oxides of magnesium and alkali metals probably originated from the walls of the glass vessel in which the PPA polymerization took place.



## OPTICALLY ANISOTROPIC DOPE STUDIES

In a further effort to find a solvent system for the AF-R-56 to produce a high-solids, good viscosity spinnable dope, an investigation of optical anisotropy (liquid crystalline behavior) of polymer solutions was undertaken. Polymers which give optically anisotropic solutions are found to assume a rod-like conformation. The possibility of the occurrence of such ordering in solutions of rigid rod-like molecules had already been predicted by Flory<sup>(4)</sup> and Onsager.<sup>(5)</sup>

Two classes of polymers which are known to form such anisotropic solutions are the poly- $\alpha$ -amides, represented by poly- $\gamma$ -benzyl-L-glutamate<sup>(6-7)</sup> and the aromatic polyamides, represented by poly(p-benzamide).<sup>(2)</sup> The mer units in poly- $\gamma$ -benzyl-L-glutamate have been found to define a helix, the overall polymer molecule thus forming a rod. As in natural polypeptides, hydrogen bonding between the individual mer units results in the helix as the most energetically stable (lowest energy) conformation. Thus, the rod-like geometry is maintained in those solutions where there is apparently not enough polarity in the solvent to disturb the hydrogen bonds.

On the other hand, the aromatic polyamides are believed to form straight rods. This is apparently the reason for the limiting statement in the DuPont patent which reads "The chain extending bonds from the aromatic rings are para-oriented and/or essentially coaxial or parallel and opposite directing."<sup>(2)</sup> Thus, although there are bond angles of less than  $180^\circ$  in both the carbonyl and the nitrogen of the amide, with parallel and opposite directing chain extending bonds, the mer units can orient such that the molecule describes a rod. The ability to assume such orientation without external fields, etc., is defined as "self-correcting".

Figures 4 and 5 show two possibilities for rod-like molecules from poly(p-benzamide). Both conformations can conveniently hydrogen bond with one another although in this case the hydrogen bonding is intermolecular. It should be noted here that comparable structures can also be composed for AA-BB polyamides as long as the distance between the AA groups is approximately the same as the distance between the BB groups. It is felt that the energy gained by hydrogen bonding in this fashion more than offsets the resonance energy lost by rotating the amide groups perpendicular to the rings. This assumption has been arrived at independently for aromatic polyamides in the solid state by Herlinger, et.al.,<sup>(8)</sup> who studied orientation in fibers by x-ray technique.

Although either the conformation pictured in Figure 4 or Figure 5 is assumed to be correct for anisotropic poly aryl amide dopes prepared in aprotic solvents such as dimethyl acetamide/lithium chloride systems, the possibility that the polymer remains completely unprotonated in such acids as hydrofluoric and sulfuric is difficult to imagine. It is postulated that the polyprotonated resin salt must become a self-correcting structure by a different mechanism. Intermolecular hydrogen bonding may be minimal or play no role at all.

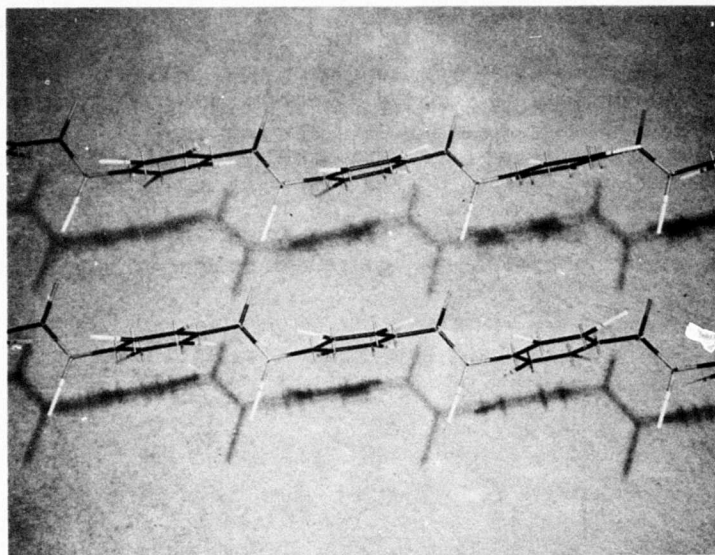


Figure 4. "Stair-Step" Self-Correcting Conformation for Poly(p-benzamide)

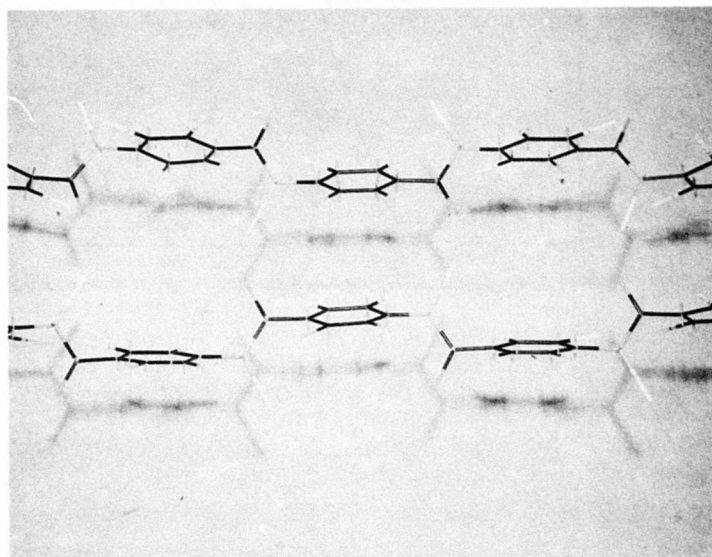


Figure 5. "Alternating" Self-Correcting Conformation for Poly(p-benzamide)

The physical properties of optically anisotropic solutions are quite pronounced. Such solutions appear to the naked eye to be turbid or hazy, yet contain essentially no undissolved solid. Another quality described for the polyamides is "stir opalescence" since if such a solution is stirred or tilted there is produced a characteristic, readily-observed, satin-like sheen or glow. Optically anisotropic solutions also possess the ability to depolarize plane polarized light and, most importantly, exhibit a marked decrease in solution viscosity as the anisotropic phase is reached. Figure 6 shows such a viscosity pattern for poly(p-benzamide) as a function of concentration. It is believed that this property may be a prerequisite to achieve adequate solids levels in order that coagulation does not severely disrupt the sought molecular alignment.

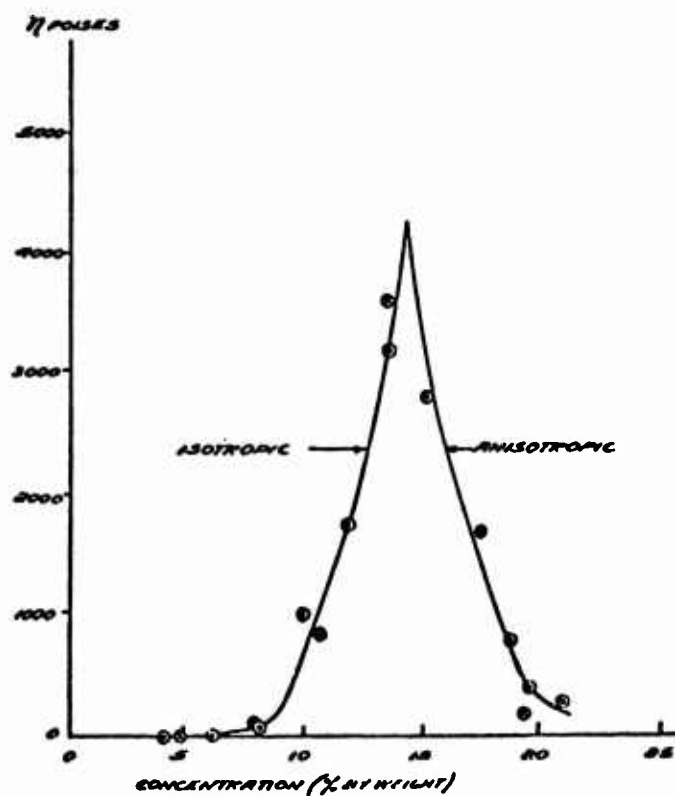


Figure 6. Viscosity as a Function of Concentration for Poly(p-benzamide) in Hydrogen Fluoride at 0°C (from Reference 2)

#### A. The AF-R-56 Polymer and Its Chlorinated Derivative

Attempts were made to ascertain whether the AF-R-56 polymer or its chlorinated derivative would form such optically anisotropic solutions. With the sole exception of formic acid or formic acid/*m*-cresol solutions, results were not forthcoming from any solvent investigated. The familiar formic acid/*m*-cresol spinning dopes begin to grow hazy at higher than 2% solids loading. "Stir opalescence" can be detected at this point but solution viscosity is still on the increase. Even higher solids loading yields either gels or undissolved particles.

Experimental results certainly indicate that the AF-R-56 molecule is rod-like. The molecular weight/intrinsic viscosity results attest to the fact that relatively small polymer molecules have high intrinsic viscosities, a result attributed to rod-like molecules in solution at infinite dilution. However, upon examination of molecular models of the polymer, the rod is found to be bent. The connecting bonds of each mer unit in the AF-R-56 polymer subtend an angle of  $150^\circ$  (Figure 7) instead of being "parallel and opposite directing" as postulated as a criteria for ordered polymer solutions in Reference 2.

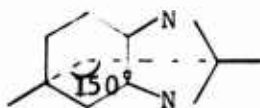


Figure 7. Geometry of AF-R-56 Mer Unit (Hydrogen Atoms, Other External Bonds and Double Bonds Not Shown to Simplify Sketch)

There is one special case in which the overall AF-R-56 polymer can define a straight rod. As Figure 8 shows, this occurs only when each mer unit mirrors the geometry of its neighbor mers. The energy requirement involved maintaining such a conformation is thought to be beyond the capabilities of the polymer. There is no convenient hydrogen bonding in this case and whatever hydrogen bonding that does occur, occurs along the plane of the rings, intermolecularly.

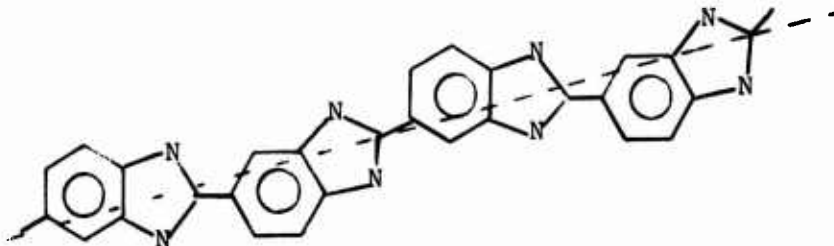


Figure 8. AF-R-56 Polymer in "Straight Rod" Conformation

The possibility does remain that in the formic acid/m-cresol solvent system, portions of the molecule may be held in just such an array by hydrogen bonding aided by electronic repulsion as shown in Figure 9.

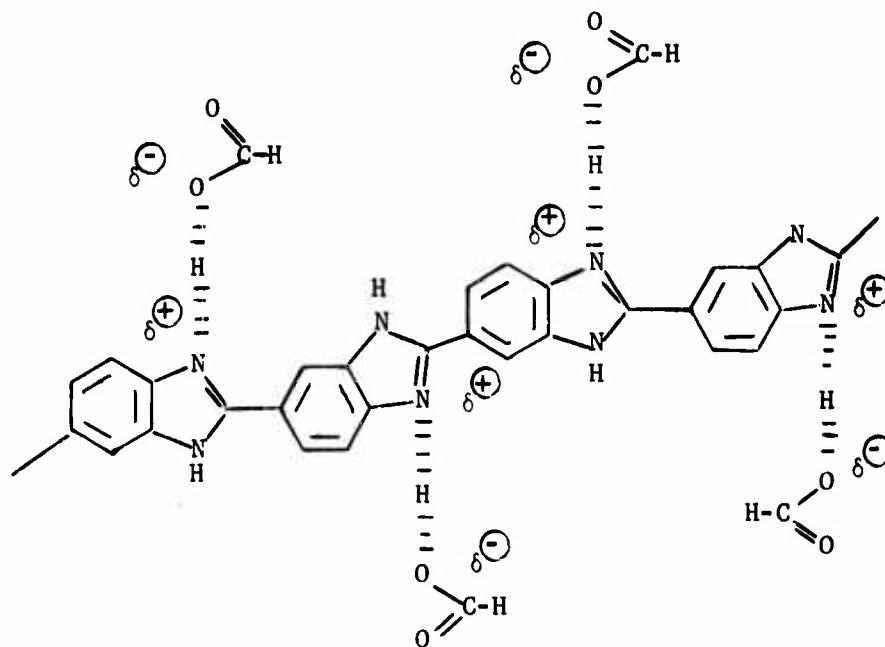


Figure 9. Possible Hydrogen Bonding to Form Self Corrected Structure in Formic Acid

The chlorinated modification of the AF-R-56 resin may be dismissed with the same arguments. Chlorination does not change the basic molecular structure. The resulting random arrangement of chlorinated and unchlorinated molecules would probably not facilitate the formation of ordered solutions.

#### B. Other Polymers

Other series of polymers were investigated during this program, to determine their ability to form optically anisotropic solution. The self-correcting concept, as applied, indicates that many other polymers can possess the necessary geometry for forming optically anisotropic solutions. However, the polymer must maintain this self-corrected conformation in the solvent. The only systems described in the literature, that are capable of doing so, are those that can hydrogen bond to reach an energy minimum in the self-corrected state or that can internally hydrogen bond to form a helix describing a rod.

Other classes of macromolecules should form optically anisotropic solutions providing the appropriate solvent systems are found. These are the molecules which geometrically describe a straight line. Thus,

there is no self-correcting aspect involved and no need to maintain the molecule in this self-corrected form to achieve optical anisotropy. Many such polymers have been previously synthesized. In general, they are infusible, insoluble and often can be formed only in low molecular weight.

### 1. Polybenzimidazoles

Besides the AB AF-R-56, three AA-BB polybenzimidazole resins were investigated. The first alternate polybenzimidazole investigated was poly(2,2'-*p*-phenylene-5,5'-bisbenzimidazole), formed from the condensation of terephthalic acid with 3,3',4,4'-tetraaminobiphenyl. The resulting polymer had an inherent viscosity of 4.62 dl/g and was found to be soluble in the same solvents the AF-R-56 polymer is soluble in. It did, however, appear to be more soluble in DMAC containing lithium chloride and less soluble in formic acid/*m*-cresol. Like the AF-R-56 there is only one conformation possible that will describe a straight rod. Also like the AF-R-56, this conformation is not energetically preferred (Figure 10).

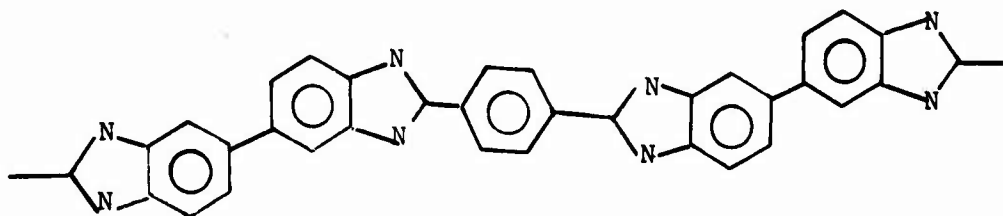
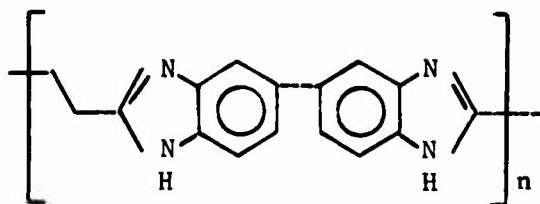


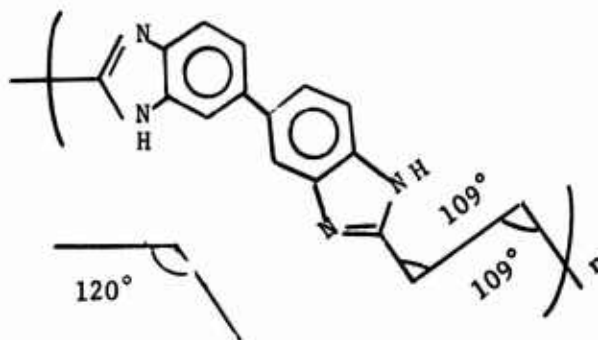
Figure 10. Chain Segment of Poly(2,2'-*p*-phenylene-5,5'-bisbenzimidazole) Showing Straight Rod Conformation

Also prepared was poly(2,2'-*m*-phenylene-5,5'-bisbenzimidazole). This polymer was prepared by the same method as the above *p*-phenylene polymer to test whether increased inherent viscosities could be obtained in polyphosphoric acid. The resulting inherent viscosity obtained (0.72 dl/g) is quite poor, but considering the structure of this molecule when compared to either the *p*-phenylene polymer or AF-R-56 this could indicate a comparable molecular weight.

The last polybenzimidazole synthesized was poly(2,2'-ethylene-5,5'-bisbenzimidazole), obtained from succinic anhydride and 3,3',4,4'-tetraaminodiphenyl. The reaction was terminated when continued heating of the polyphosphoric acid solution at 200°C gave no further increase in solution viscosity. The inherent viscosity of the final polymer was 0.87 dl/g (0.5% in H<sub>2</sub>SO<sub>4</sub>).



Investigation of the molecular geometry of this polymer indicates that even if the ethylene group could be maintained in the lowest steric energy profile, the molecule is not self-correcting as again there is an angle of up to  $120^\circ$  between the neighboring benzimidazole groups.



The polymer was found to be quite soluble in both 80:20 formic acid/m-cresol (19.8%) and in DMAC containing 8% lithium chloride (17.8%) as well as formic acid (12%) and 96%  $\text{H}_2\text{SO}_4$  (6.5%+). No evidence of optical anisotropy was observed.

## 2. Polyimides

It was felt that true self-correcting structures could be better obtained if one built polyimides using pyromellitic dianhydride (PMDA). Initially investigated was the polymer resulting from the reaction of PMDA with ethylene diamine (Figure 11).

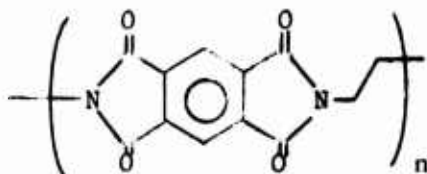


Figure 11. Poly(N,N'-ethylenepyromellitic diimide)

The reaction was run in both DMAC neat and DMAC containing lithium chloride at solids concentrations of 5% and 15%. In all cases, either the amic acid or another intermediate precipitated from solution to give a white curdy precipitate before heating. After a brief heating under reflux to complete polyimide ring closure, there was isolated in all cases a pale tan powder with an inherent viscosity of approximately 0.1 dl/g.

One other polyimide was prepared under the program. This was the self-correcting azo polyimide, poly[N,N'-(4,4'-azodiphenylene)-pyromellitic diimide] (Figure 12).

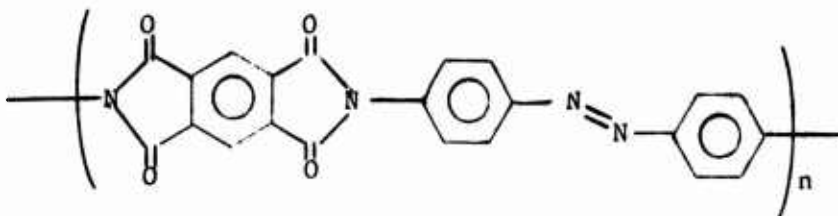


Figure 12. Poly[N,N'-(4,4'-azodiphenylene)-pyromellitic diimide]

The amic acid of this polymer was a deep purple color and was quite soluble in the solvent in which it was prepared (8% in DMAC containing 8% lithium chloride). Heating this solution under reflux produced an insoluble red powder. This work is analogous to the recently published work by Bach and Hinderer<sup>(9)</sup> in which they prepared and spun the amic acid dope of the polyazoimide pictured in Figure 13 to give, after heat stretching, a fiber with tenacity 3.9 g/den and a tensile modulus of 288 g/den.



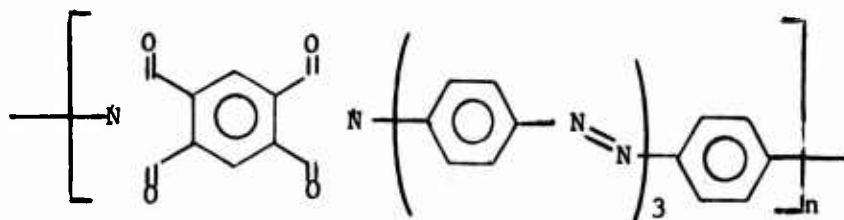


Figure 13. Structure of Polyazoimide Molecule Produced by Bach and Hinderer

Attempts were also made to prepare an imide containing monomer with which to prepare self-correcting polymers. The desired compound was not obtained cleanly from the condensation of pyromellitic dianhydride with an excess of *p*-phenylene diamine. Instead, the light tan material obtained showed no tendency to melt through 405°C, and was soluble in hot DMAC and ethanol. An infrared spectrum indicated that the desired bisimide was not formed.

### 3. Polyazomethines

Polyazomethines or poly-Schiffs bases can be synthesized to satisfy the requirements for "self-correcting" polymers provided both the dialdehyde and the diamine chosen have their functional groups "parallel and opposite directing". Aromatic polyazomethines also have another advantage in that they are professed to be thermally stable. These polymers have been investigated and high molecular weight polyazomethines are reportedly soluble in a mer-like solvent, benzylidene-aniline.<sup>(10 a-b)</sup> Subsequent to this, other workers have claimed that the techniques used by D'Alelio did not result in polyarylazomethines but instead to decomposition products which probably consisted of "crosslinked, condensed, heteroaromatic compounds of very uncertain structure."<sup>(11)</sup> Polymeric Schiff's bases of increased molecular weight were produced by placing another functionality on the dialdehyde in order to render it and the resultant polymer soluble in compatible solvents.<sup>(12)</sup>

Attempts to prepare "self-correcting" polyarylazomethines led, in our hands, to yellow to yellow-orange polymers of low molecular weight. In these cases the reactants were terephthaldehyde (recrystallized from benzene) and *p*-phenylene diamine (recrystallized from benzene). Polymerizations were conducted in toluene, *N*-methyl pyrrolidinone and *N*-methyl pyrrolidinone containing 4% lithium chloride. The resultant "polymers" were insoluble in all solvents except those that were strongly acidic (formic acid, trifluoroacetic acid) and hot *N*-methylformamide.

Attempts to dissolve the polymer in benzylidene aniline<sup>(13)</sup> were unsuccessful. This may be due to an end group effect as our polymer is chain terminated with aryl amines and is unlike the polymers with benzene ring termination produced by D'Alelio by the bis-exchange method.

The literature<sup>(12)</sup> suggests that in addition to the hydrolytic instability of aromatic Schiff's bases, low molecular weights are observed in the polymers due to the slow reactivity of the second amine when two amine groups are present on the same ring. Thus, the azo structure has a deactivating effect on the second amine and this further inhibits molecular weight growth.

An attempt was made to prepare and isolate the diamine-bis Schiff's base, prepared from terephthaldehyde and an excess of p-phenylene diamine. The resultant product had the same color, melting point (none through 400°), and solubility characteristics as the previously described polymer obtained from the stoichiometrically condensed monomers. Either the low molecular weight polymer previously isolated is only a trimer composed of one aldehyde unit and two amine units, or a low molecular weight polymer formed from this nonstoichiometric reaction. An alternate unequivocal method of preparing the trimer was also briefly investigated. This consisted of reacting one mole of terephthaldehyde with two moles of p-nitroaniline followed by reduction of the nitro groups. The bis-nitro compound was prepared by the method of D'Alelio<sup>(10-b)</sup> to give a bright yellow crystalline compound, mp 265°-268°C. An attempt to reduce this compound with sodium thiosulfite led to recovered starting material.

### SECTION III EXPERIMENTAL

#### 3,4-DIAMINOBENZOIC ACID (DABA)

Crude DABA was purchased from American Hoechst Corporation and Aldrich Chemical Company. It was received as a tan powder with mp from 200° to 208°C, depending on the lot. It was conveniently purified to polymer grade material by dissolving in dilute aqueous hydrochloric acid, treating the solution with activated charcoal, filtering and adding more hydrochloric acid to the colorless filtrate until the monohydrochloride salt precipitated. This salt was found to be only very slowly hygroscopic and quite stable to air oxidation. Quality control was run by means of a neutralization equivalent.

#### AF-R-56

The self-condensation of DABA in polyphosphoric acid and subsequent preparation of the spinning dope was conducted in the following manner.

##### A. Preparation of Polyphosphoric Acid

Polyphosphoric acid of the desired concentration needed for optimum condensation, was prepared by mixing phosphorus pentoxide with phosphoric acid. Thus, in a typical preparation, 7470 g (52.6 mole) of phosphorus pentoxide (Stauffer) was weighed out into a 12  $\ell$  flask under a nitrogen atmosphere. To this was added 5000 g of 85-87% phosphoric acid (Allied Chemical) and stirring was initiated. The temperature was adjusted to 110°C and held at that temperature until dissolution occurred. Phosphorus pentoxide content of the resulting polyphosphoric acid was analyzed by measuring the index of refraction.<sup>(15)</sup> For this batch, analysis indicated a P<sub>2</sub>O<sub>5</sub> content of 84.1  $\pm$  0.5%, labeled 2225-13-A3.

##### B. Polymerization

To the above polyphosphoric acid solution was added 249.4 g of the purified monohydrochloride salt of diaminobenzoic acid at such a rate that dissolution occurred at a temperature of 100°C (the addition took 2 days). After complete dissolution, the flask (under nitrogen) was placed in an oven and allowed to stand at 180°C for 2 hours, 200°C for 4 hours, and 220°C for 17 hours. While still hot, the PPA solution was mixed with water in a large Waring blender and the aqueous solution was allowed to soak for 56 hours. The resin was filtered and treated with 6  $\ell$  of concentrated aqueous ammonia under reflux for 16 hours. The ammonia solution was replaced with a fresh batch and boiling under reflux continued for 16 additional hours. The polymer was then filtered, washed with water until neutral, dried and milled to give 133.0 g of tough, yellow fibrous material,  $\eta_{inh}$  15.3 g/dl, 2225-14-A9.

### C. Spinning Dope Preparation

To 800 g of formic acid (Aldrich 97+%, redistilled, contained 0.8% water) and 200 g of m-cresol (redistilled, 0.5% water) in a 2 l resin kettle equipped with a shear stirrer, was added slowly and under dry nitrogen, 17 g of the above polymer, keeping a constant solution temperature of 1.0°C. Dissolution time was 20.5 hours. The solution was degassed and stored until needed for spinning, labeled 2239-6-A4.

### CHAIN TERMINATED AF-R-56 POLYMER

To 12,470 g of polyphosphoric acid (85%  $P_2O_5$ ) was added 250 g (1.325 mole) of 3,4-diaminobenzoic acid monohydrochloride and 0.6344 g (0.00520 mole) of primary standard benzoic acid. The solution was stirred at 100° for three days until all of the monomers dissolved. The temperature was then raised to 180° for 2 hours, 200° for 5 hours, and 220° for 18 hours. After standard workup and purification procedures, a yellow-green polymer,  $\eta_{inh}$  2.72 (0.5%  $H_2SO_4$ ) was obtained. From amount of reagents added, assuming end capping to be quantitative, a D.P. of 255 and a molecular weight of 29,560 was calculated.

### CHLORINATION OF AF-R-56

To 2000 g conc.  $H_2SO_4$  under nitrogen was added 10 g of AF-R-56 (Batch 2225-26-A10,  $\eta_{inh}$  16.8) and 4.0 g of iodine. The nitrogen was then replaced with chlorine gas which was introduced under the surface of the solution for 18 hours. The sulfuric acid solution was then drowned in a 40% sodium thiosulfate solution and the polymer isolated by filtration. The polymer was then repeatedly washed with water and finally dried to constant weight under vacuum. Analyses indicated the polymer had an inherent viscosity of 6.0 and a chlorine content of 13.1%.

### AA-BB POLYBENZIMIDAZOLES

#### A. Poly-2,2'-(p-phenylene-5,5'-bisbenzimidazole)

Two hundred grams of prepared polyphosphoric acid, analyzing at 83.4  $\pm$  0.5%  $P_2O_5$ , under nitrogen in a 250 ml resin kettle was charged with 1.980 g (0.01193 mole) terephthalic acid. The solution was heated to 115°C and stirred for 72 hours in an attempt to dissolve the acid in the PPA. To this mixture was then added 2.553 g (0.1193 mole) of polymer grade diaminobenzidine and the solution was allowed to stir at 180°C for three weeks. It was then heated to 230°C in an effort to effect dissolution of the last of the terephthalic acid, held at 210°C for 5 days, 180°C for 3 more days, and finally brought up to 230°C overnight, after the last of the terephthalic acid had finally dissolved. The PPA solution was worked up as above to give a tough brownish-green polymer,  $\eta_{inh}$  4.6 dl/g.

	<u>% C</u>	<u>% H</u>	<u>% N</u>	<u>% P</u>
Calculated for $C_{20}H_{12}N_4$ :	77.91	3.92	18.17	0.00
Found:	77.56	4.11	18.05	0.042

B. Poly(2,2'-m-phenylene-5,5'-bisbenzimidazole)

To 1.66 g (0.0100 mole) of isophthalic acid (from methanol) in a 500 ml resin kettle was added 270 g of polyphosphoric acid (83.4  $\pm$  0.5%  $P_2O_5$  content by analysis). The mixture was allowed to warm to 140°C for 2 hours and 180°C for 30 minutes. The temperature was reduced to 140°C and the 3,3',4,4'-tetraaminobiphenyl (2.14 g, 0.0100 mole) added. The temperature was increased to 180°C for three days, and 225°C for an additional day. The solution was worked up in the usual method to give 1.4 g of pale green powder,  $\eta_{inh}$  0.72 dl/g.

C. Poly(2,2'-ethylene-5,5'-bisbenzimidazole)

To 200 g of PPA (83.4  $\pm$  0.5%  $P_2O_5$ ) in a 300 ml resin kettle was first added 2.1495 g (0.010032 mole) of recrystallized polymer grade 3,3',4,4'-tetraaminobiphenyl, followed by approximately one-half of the 1.0054 g (0.010047 mole) succinic anhydride. The solution was allowed to stir at 100°C for two hours before the final portion of succinic anhydride was added. The temperature was maintained at 110°-150°C for two days, then inadvertently raised to 305°C by a malfunctioning heater on the third day. The solution was then cooled and the inherent viscosity measured,  $\eta_{inh}$  0.73 dl/g. It was worked up after an additional 24 hours @ 220°C to give 2.21 g of white powder,  $\eta_{inh}$  0.87 dl/g.

AA-BB POLYIMIDES

A. Poly(N,N'-ethylene pyromellitic diimide)

To 85.0 ml of dimethylacetamide in a 250 ml one-necked flask equipped with a magnetic stirring bar was added 10.9 g (0.0500 mole) of pyromellitic dianhydride and the flask was closed with a stopper connected to a serum cap. Ethylene diamine (3.00 g, 0.050 mole) was then added through the serum cap to the solution below. Immediately a white gel separated from the solution. After standing overnight, attempts were made to dissolve the gel by first chilling and then warming the solution. Finally, the mixture was heated under reflux for 2 days to yield, after filtration, a brown powder,  $\eta_{inh}$  0.11 dl/g.

B. Poly[N,N'-(4,4'-azodiphenylene)pyromellitic diimide]

To 4.12 g (0.020 mole) of 4,4'-diaminoazodiphenylene in 100 ml of N-methylpyrrolidinone containing 8% lithium chloride in a three-necked 250 ml flask equipped with a magnetic stirring bar and a nitrogen inlet, was added 4.36 g (0.020 mole) of pyromellitic dianhydride. The solution

was allowed to stand at room temperature. There was no precipitate and the solution was of a watery viscosity. After three days, the solution was heated under reflux to yield a fine red insoluble powder.

C. N,N'-Bis(p-aminophenyl)pyromellitic Diimide

To 10.8 g (0.1 mole) of p-phenylene diamine (recrystallized from benzene) in 100 ml of N-methylpyrrolidinone was slowly added 2.18 g (0.01 mole) of pyromellitic dianhydride. The solution was allowed to stir at room temperature overnight, then heated under reflux for 4 hours and allowed to cool. As nothing precipitated, the solution was drowned in 1500 ml of water and filtered.

To separate the product from the excess p-phenylene diamine the filtered material was washed with ethanol and finally recrystallized from dimethylacetamide to give 1.74 g of a pale tan powder which did not melt through 405°C. An infrared spectrum of the material indicated that this product consisted of both the uncyclized amic acid and the imide. No further attempt was made to purify or cyclize the material.

POLYAZOMETHINES

A. Poly Schiff's Base from Terephthaldehyde and p-Phenylene diamine

To a solution of 5.4 g (0.050 mole) of p-phenylene diamine in 200 ml of dimethylacetamide containing 4 g of lithium chloride was added 6.7 g of terephthaldehyde and the solution was heated under reflux overnight to give a yellow powder. This powder was found to be soluble only in formic acid and trifluoroacetic acid. This powder was believed to be of very low molecular weight.

## SECTION IV REFERENCES

1. Walter P. Fitzgerald, Chadwick B. Delano, R. Randolph Doyle, "High Strength, High Temperature Polymeric Fibers", AFML-TR-72-211, Contract No. F33615-71-C-1435, September 1972.
2. S. L. Kwolek (DuPont) U.S. 3,671,542 (1972).
3. P. J. Flory, "Principles of Polymer Chemistry", Cornell University Press, Ithaca, N.Y., 1953, p 310ff.
4. P. J. Flory, Proc. Royal Soc., (London) A234, 73 (1956).
5. L. Onsager, Ann. N.Y. Acad. Sci., 56, 627 (1949).
6. C. Robinson, J. C. Ward, R. B. Beevers, Disc. Faraday Soc., 25, 29 (1958).
7. J. Hermans Jr., "Ordered Fluids and Liquid Crystals", Advances in Chemistry, No. 63, 282 (1967).
8. H. Herlinger, H. Knoell, H. Menzel and J. Schlaefer, "High-Temperature and Flame Resistant Fibers," Applied Polymer Symposia 21, 215 (1973).
9. H. C. Bach and H. E. Hinderer, "High-Temperature and Flame Resistant Polymers," Applied Polymer Symposia 21, 35 (1973).
- 10a. G. F. D'Alelio, et al., J. Macromol. Sci. (Chemistry) A1[7] (1967) 1161, 1259, 1279, 1299, 1321, 1331.
- 10b. Ibid., 1251.
11. J. H. Hodgkin and J. Heller, Macromolecules 2[5] 556 (1969).
12. J. H. Hodgkin and J. Heller, J. Poly. Sci., C[29] 37 (1970).
13. Org. Syn., Coll. Vol. I, 80.
14. J. Higgins, J. F. Jones and A. Thornburgh, Macromolecules 2[5] 558 (1969).
15. R. G. Downing and D. E. Pearons, J. Am. Chem. Soc., 83, 1718 (1961).

UNCLASSIFIED

Security Classification

## DOCUMENT CONTROL DATA - R &amp; D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author) WHITTAKER CORPORATION Research and Development Division San Diego, California 92123		2a. REPORT SECURITY CLASSIFICATION Unclassified	
		2b. GROUP --	
3. REPORT TITLE High Strength, Thermally Stable Polymeric Fibers			
4. DESCRIPTIVE NOTES (Type of report and inclusive dates) Technical Report AFML-TR-74-22, 1 July 1972 to 1 September 1973			
5. AUTHOR(S) (First name, middle initial, last name) Chadwick B. Delano R. Randolph Doyle Robert J. Milligan			
6. REPORT DATE February 1974		7a. TOTAL NO. OF PAGES 38	7b. NO. OF REFS 15
8a. CONTRACT OR GRANT NO. Contract F33615-72-C-1458		9a. ORIGINATOR'S REPORT NUMBER(S) Whittaker Report No. MJO 3039 Technical Report	
b. PROJECT NO.		9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report) AFML-TR-74-22	
c.			
d.			
10. DISTRIBUTION STATEMENT Distribution limited to U.S. Government agencies only; test and evaluation; August 1973. Other requests for this document must be referred to the Air Force Materials Laboratory, Nonmetallic Materials Division, Composite and Fibrous Materials Branch, AFML/MBC, Wright-Patterson AFB, Ohio 45433.			
11. SUPPLEMENTARY NOTES --		12. SPONSORING MILITARY ACTIVITY Air Force Materials Laboratory, Nonmetallic Materials Division, Composite and Fibrous Materials Branch, Wright-Patterson AFB, Ohio 45433.	
13. ABSTRACT The subject program has been concerned with the synthesis of specifically ordered heterocyclic polymer systems for evaluation as high tenacity fiber candidates. Specifically sought in the performance spectrum of successful fibers was a high level of mechanical properties, high energy absorption (work-to-break) and high temperature performance. The primary structural criteria for polymer order were: chain growth which describes a straight line; the absence of bulky pendant groups; capability for approaching a planar structure and interchain bonding. These structural features, which are primarily responsible for providing enhanced thermal and mechanical capability relative to non-oriented counterparts, at the same time render the polymer system highly intractable. The exception to these criteria appears to be the formation of the sought rod geometry through appropriate solvation of macromolecules containing flexible links to obtain for instance a helix. Efforts with the poly-2,5(6)benzimidazole (AF-R-56) did not produce a yarn whose properties exceeded the previous contract yarn strengths of: as spun T/E/Mi = 7.4 gpd/30%/97 gpd; drawn T/E/Mi = 13.2/2.2/501. It is thought that low solids content dopes used in yarn formation present peculiar difficulty in the attainment of a higher strength yarn. Achievement of higher solids concentration in the dopes for yarn formation should provide enhanced yarn properties from the AF-R-56. This solids "barrier" problem is solved when liquid crystalline behavior can be achieved with the macromolecules since the viscosity of solution reduces with increasing solids concentration in the anisotropic state. Efforts to induce the AF-R-56 into liquid crystalline behavior showed only slight promise.			



14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Fibers from ordered heterocyclic aromatic polymers systems Wet spinning of the 2,5-polybenzimidazole polymer High tenacity fibers						

AD 918 253

AUTHORITY:

AFU AL ltr.

15 OCT 82

